

**STUDIES ON SYNTHESIS, CHARACTERISATION AND
BIOLOGICAL ACTIVITY OF SOME NOVEL HETEROLIGAND
COMPLEXES OF Ni (II), Cu (II) AND Co (II)**

A THESIS

**SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
OF**

**BUNDELKHAND UNIVERSITY
JHANSI**

DECEMBER 2002



Under the Supervision of :
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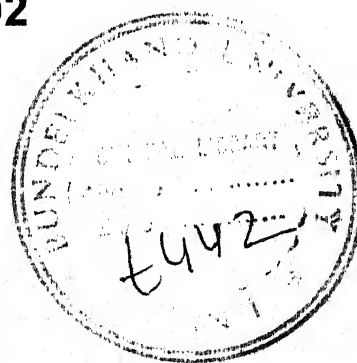
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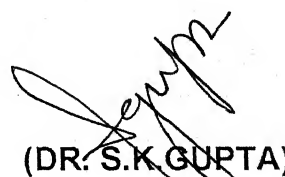
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CERTIFICATE

It is to be certified that the work presented in the thesis entitled," STUDIES ON SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF SOME NOVEL HETEROLIGAND COMPLEXES OF Ni (II), Cu (II) AND Co (II)," has been carried out under my guidance and supervision by SMT. ANSHU SEHGAL, M.Sc., herself for the degree of Doctor of Philosophy in Chemistry of Bundelkhand University, Jhansi.

I further certify that the work and the approach adopted by the investigator is entirely original and it has neither been carried out anywhere else in the same form and manner nor it has been submitted for any other degree of this or any other university.

SMT. ANSHU SEHGAL has put in more than 200 days of work in the Postgraduate Department of Chemistry of Bipin Behari College, Jhansi, (U.P.).



(DR. S.K. GUPTA)

Department of Chemistry
Bipin Behari College, Jhansi

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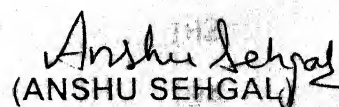
I sincerely acknowledge the constant support and blessings of my respected parents-in-law Smt. Chandrakanta and Shri Hari Ram Sehgal who have provided to me encouragement and support throughout the tenure of the investigations.

I am also very thankful to my parents Smt. Saroj and Shri R. K. Vasudev for their emotional support during the period of this research. My younger brother, Rahul Vasudev and my younger sister, Purna Vasudev, too chipped in with his assistance and cooperation, when it mattered most, at the time of typing of this thesis.

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DATED : December , 2002


(ANSHU SEHGAL)

LIST OF CONTENTS

Chapter	Section/subsection	Title/subtitle	Page
I	1.0	Introduction	1
	1.1	Prelude	1
	1.2	Literature survey	4
	1.3	Plan of work	9
		References	17
ii	2.0	Physicochemical analysis	26
	2.1	Electronic Spectra	26
	2.2	Infra Red Spectra	34
	2.3	Magnetic Studies	38
		References	47
III	3.0	Synthesis, elemental analysis And Microbial Studies	50
	3.1	Synthesis of ligands	50
	3.2	Synthesis of ternary complexes	52
	3.3	Elemental analysis and molecular Formula	61
	3.4	Microbial Studies	62
		References	75
IV	4.0	Ternary complexes of copper (II)	78
	4.1	Electronic Spectral Studies	78
	4.2	Infra Red Spectral Studies	82
	4.3	Magnetic Studies	109
		References	118
V	5.0	Ternary complexes of copper (II)	120
	5.1	Electronic Spectral Studies	120
	5.2	Infra Red Spectral Studies	124
	5.3	Magnetic Studies	148
		References	155
VI	6.0	Ternary complexes of copper (II)	156
	6.1	Electronic Spectral Studies	156
	6.2	Infra Red Spectral Studies	160
	6.3	Magnetic Studies	184
		References	192
VII	7.0	Microbial Studies	194

CHAPTER - 1

CHAPTER - I

INTRODUCTION

1.1 Prelude

It is well known that the coordination of a metal ion with only one type of ligand leads to the formation of a binary or a simple complex system depending upon the coordination number of the metal ion under investigation. However, in the case of the coordination of the metal with two different types of ligands, a mixed or more specifically a ternary complex¹ is formed.

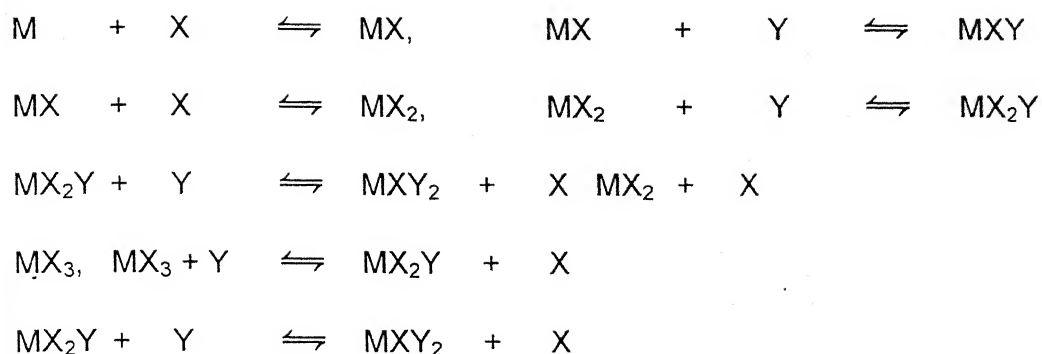
There are three important routes for the formation of such ternary complexes in solution as enumerated below:

(a) **Simultaneous addition:** It is observed that if two different ligands of comparable coordinating ability are added simultaneously to a solution of a metal, both the type of ligands coordinate simultaneously to yield mixed complexes with 1:1:1, 1:2:1 or 1:1:2 ratios. Thus,

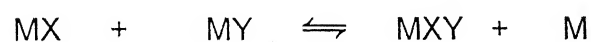


(b) **Stepwise formation:** In contrast to the first route, stepwise ternary complex formation occurs when two ligands of adequately different coordinating ability are added to a metal ion solution in order of their increasing complexing ability.

Thus,



(c) Combination of two binary complexes: When solutions of two binary complexes are added together, there is the possibility of formation of a ternary complex in solution:



In all the above equilibria, charges have been ignored for convenience.

In practice, the possibility of formation of a binary, ternary or higher complex (quaternary and so on) is determined mainly by considerations such as the standard electrode potential of the metal, its size as well as basicity and denticity of the ligand selected for the study of phenomenon of complex formation. In addition, a number of other influences such as the nature of the coordinate bond², extent and type of chelate formation³ and shape⁴ and the

configuration⁵ of the complex formed also affect the formation of simple and the mixed complexes.

The greater stability of the ternary complexes compared to their binary counterparts is influenced by a number of other factors⁶⁻⁹ too. The more prominent among them are the following:

- (i) Nature of bonding in ligands
- (ii) Ionic strength of the medium
- (iii) pH of the solution
- (iv) Temperature
- (v) dielectric constant of the medium

The greater stability of ternary complexes vis-a-vis binary complexes has been proposed to be explained by a polarized ion model by Marcus et al¹⁰⁻¹². On the basis of this model, it has been possible to determine force constants; energy and thermodynamic parameters as well in the ternary complex formation equilibria in solution¹³⁻¹⁵.

There is no denying the fact that in general, the stability constants of mixed complexes are greater than the corresponding binary complexes. A number of techniques have been utilized to evaluate the stability constants of ternary complexes. Thus, electrometric^{16, 17}, spectrophotometric¹⁸, liquid-liquid extraction¹⁹ and phase distribution methods²⁰ are most commonly employed for the purpose. Magnetic susceptibility measurements, IR, EPR and NMR spectra and thermal properties better investigate the other aspects of hetero ligand complexes as we shall see later in the chapter.

1.2 Literature survey

Ligands with atoms of oxygen, nitrogen and sulphur elements as donor atoms attached to them are of great importance because these elements are found in all biological systems. Further, of greater importance to us are the biologically active neutral bases.

Chelates i. e. complexes with ligands forming ring structures with metals have been found to be of great significance in the diverse fields of analytical chemistry²¹, medicine²², biology²³, and industry²⁴.

Before we describe the actual investigations carried out by us, it would be worthwhile to review the work that has already been done in the field and the methods employed for the purpose by different investigators. Besides, a description of methods employed by us would follow in the next chapter.

A chelate of a suitable metal ion with 8-hydroxyquinoline serves as a useful anti-fungal and antibacterial agent²⁵. Oxime metal chelates have been found to be anti microbial agents²⁶. Chelates with organic ligands containing -N, -NH₂, -OH, -SH and -COOH groups as coordinating ligands are found to reduce damage to organs exposed to radiations²⁷. It has also been observed²⁸⁻³⁶ that ligands with nitrogen as the coordinating site exhibits significant microbial activity.

Malik, Singh and Tandon³⁷ have investigated the binary and ternary complexes of some aminopolycarboxylic acids. A number of other investigators³⁸⁻⁴⁰ employed ligands, which are used as medicine in the normal course to form complexes with transition metal ions. Some examples of such

ligands are penicillin, penicillinamine and dextran. The complexes so formed were the basis of a number of clinical trials.

Metal chelates have made tremendous contribution towards the development of analytical chemistry.

Agarwal⁴¹ has successfully employed N-hydroxy-N-phenylformalidine to quantitatively analyze copper (II) and nickel (II). On similar lines, Patel and coworkers⁴² have used 7-nitro-8-quinolinol-5-sulphonic acid as a reagent to estimate copper (II) and iron (III) in solution.

It has been found more useful to classify the metal chelates on the basis of number of ligands linked to the central metal ion for the understanding of the vast field encompassed by such coordination compounds in various aspects for which they have been found useful in analytical chemistry. A brief description of each class follows:

- a) Binary chelate complexes: these types of complexes have found extensive and widespread use in photometry⁴³⁻⁴⁵ and ion exchange methods.
- b) Ternary chelate complexes: these types of complexes have been used in catalytic and complexometric titrations⁴⁹⁻⁵⁵.
- c) Quaternary chelate complexes: Among this class of complexes, which are mostly of academic interest, are the hetero ligand complexes of transition metals and lanthanides⁵⁶⁻⁶⁴.

d) Bimetal bridge metal complexes: In such complexes a single ligand molecule is linked to the two metal atoms of the same or different metals in the same/different oxidation state. Such complexes are in general, coloured and hence useful in colourimetric analysis⁶⁵⁻⁶⁸.

Magnetic measurements, infra red and electronic spectral studies have been intensively and extensively applied to elucidate and establish the nature of bonding and structure of ternary metal complexes. In fact, we have also used this approach in combination with chemical assay to determine the molecular formula.

A survey of literature reveals that studies⁶⁹⁻⁷⁷ on neutral ligand complex formation have registered a considerable increase over the past few years. Due to a variety of coordination shapes assumed by copper (II) complexes, a number of investigators⁷⁸⁻⁸⁴ have directed their attention to study the complexes of this metal.

The structure of mixed ligand complexes of some transition metal ions and rare earth metals with 4,4'-bipyridyl and 2,9-dimethyl-1, 10-phenanthroline have been elucidated by a number of workers⁸⁵⁻⁹¹. Czakis and Danuta⁹² isolated the 2,2'-dipyridyl and 4,4'-dipyridyl complexes with halides as the other ligands. Their studies were based on the infra red spectral studies of these mixed complexes. Ahuja and Singh⁹³ have prepared cobalt (II), nickel (II), zinc (II), cadmium (II) and mercury (II) thiocyanates with 4,4'-dipyridyl and investigated them spectroscopically to find that that 1:1 ratio is the norm for metal to 4,4'-dipyridyl molecule while the remaining coordination positions are occupied by the other ligand. Further they found that bridging polymeric species are formed and

both the ligands can act as bridging ligands. M. Camo et al⁹⁴ synthesized and investigated the donor acceptor compounds of mercury (II) with cyanide as one ligand and 2,2'-bipyridyl, 1,10-phenanthroline and 2,9-dimethyl-1, 10-phenanthroline separately as the other ligand. They undertook extensive infra red spectral studies of these ternary complexes. On the other hand Melnik et al⁹⁵ have synthesized 4,4'-bipyridyl adducts with copper (II)-isobutyrate. The adducts were found to be binuclear with 4,4'-bipyridyl linking the two copper (II) ions through their nitrogen atoms.

Thomas and coworkers⁹⁶ have studied the complexes of copper (II) with 2,2'-bipyridyl and 2,9-dimethyl-1, 10-phenanthroline. Kwik and coworkers⁹⁷ have gone on to investigate copper (II) ternary complexes of o-phenanthroline with O-donor ligands which form chelate rings. They found that with increase in size of the chelate ring, Cu (II)—O bond gets weaker. This was indicated by infra red spectral studies. The same investigators⁹⁸, in a separate report, have described the magnetic moment, IR, ESR and polarographic studies of copper (II) ternary complexes of 2,2'-bipyridyl and 1,10-phenanthroline with amino acids such as glycine, alanine, valine, tyrosine etc. Foulds and co workers⁹⁹ and Dutta and Bhattacharya¹⁰⁰ have isolated and characterized the ternary complexes of cobalt (II) with 2,2'-dipyridine, ethylenediamine, propylenediamine etc. with ligands having NN, OO, and NO as donor pairs.

Shukla and Rajkamal¹⁰¹ have investigated the hetero ligand complexes of copper (II) and cobalt (II) with phthalic acid and aromatic amines and diamines. On the other hand, Padhy and Patel¹⁰² have reported the isolation, characterization and other studies on similar complexes of nickel (II) with S and

N donor ligands like naphthylurea, 1,10-phenanthroline, 3,5-lutidine, piperidine and benzylamine.

The mixed ligand complexes of oxovanadium with dipicolinic acid and some monobasic ligands have been carried out by Kapoor et al¹⁰³. Walten and Michel¹⁰⁴ have applied the tool magnetic susceptibility to investigate the copper (II) complexes with PDA. They carried out investigations on nickel (II) ternary complexes with dipicoline and mono-, di- and tridentate N donor ligands like pyridine, α -picoline, 2,2'-bipyridine and 1,10-phenanthroline. Invariably, six coordinate complexes were formed.

The neutral complexes of lanthanides with picolinic acid-N-oxide have been prepared and investigated by Navneetham and coworkers¹⁰⁵. There was bidentate bonding of the ligand with La, Pr, Nd, Ho and Yb with the coordination number of six in each case.

Saxena and Srivastava¹⁰⁶ have contributed by study of synthesis of cobalt(II), nickel(II) and copper(II) with some Schiff's bases and testing them for their antibacterial properties.

The studies of applications of complexes useful in the biological¹⁰⁷⁻¹⁰⁸ and pharmaceutical¹⁰⁹ fields have picked up during the last few years. A number of investigators¹¹⁰⁻¹¹⁶ have taken up the study of mixed ligand complexes in the solid state using a variety of techniques such magnetic studies, IR, electronic, NMR, EPR spectral analysis and thermogravimetry. Many references are also available on the various attempts made to study the biological activity of the ternary complexes¹¹⁷⁻¹²⁸.

However, it has been observed that the study of ternary complexes of copper (II), nickel (II) and cobalt (II) in the solid state still has a substantial scope from the point of view IR spectral studies. Such studies in the solid state have been investigated to a limited extent due to the difficulty in IR spectral assignments in large molecules, which ternary complexes necessarily are because of obvious reasons. Such large molecules have a large number of vibrations and it becomes cumbersome and time consuming to interpret the structures. Further, it is not possible to obtain the Raman spectra due the fact that such complexes are insoluble in different solvents.

It was, therefore, thought worthwhile to further explore this inadequately worked out arena and make an attempt to synthesize some new ligands, investigate their structure and in combination with other suitable ligands prepare a series of ternary complexes of copper, nickel (II) and cobalt (II) in the solid state, establish their structures and carry out microbial studies to assess their biocidal activity. Thus, in short, syntheses, characterization and the study of their biological action on certain microorganisms like fungi and bacteria were carried out in a systematic manner and reported in later chapters.

1.3 Plan of work

The elemental analysis, IR and electronic spectra in conjunction with magnetic susceptibility measurements were used for characterization purposes.

Nickel (II), copper (II) and cobalt (II) were used as the central metal in for the ternary complexes under investigation.

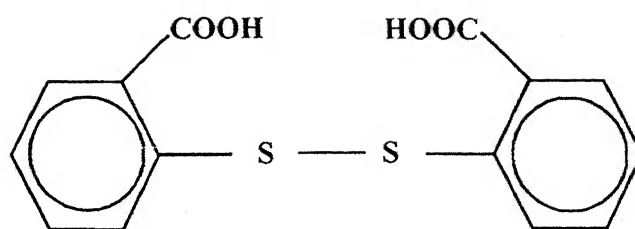
3,3'-dipyridyl(dipy.) and 4,7-dimethyl-1, 10-phenanthroline (phen.) were separately used as one of the ligands.

Four novel compounds (Figure 1.01) synthesized had two replaceable hydrogen atoms and a coordinating N and S as well. The four synthesized compounds are:

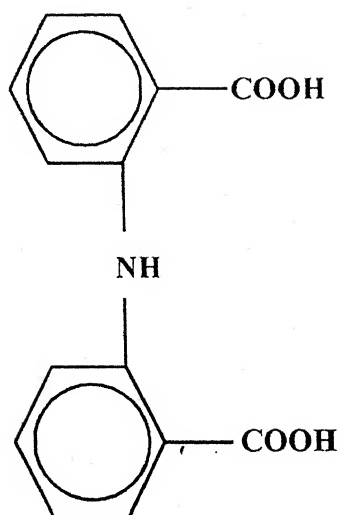
- (i) Diphenylamine-2, 2'-dicarboxylic acid (DPDC)
- (ii) 2-hydroxybenzilidine-2-aminothiophenol (HBAT)
- (iii) 2,2'-dithiosalicylic acid and (DTSA)
- (iv) 2-hydroxybenzilidine-anthranilic acid (HBAA)

In addition, the following compounds were selected to act as ligands in view of their biological importance:

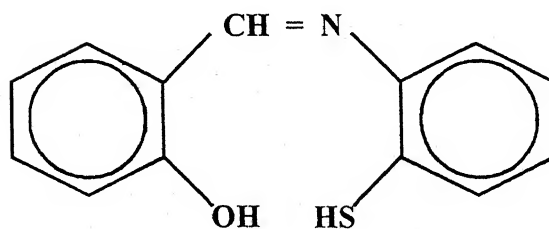
- (i) 2-mercaptobenzoic acid (MBA)
- (ii) Thiodiacetic acid(TDAA)
- (iii) 2,2'-dithiosalicylic acid(DTSA)
- (iv) Dithiopropionic acid(DTPA)
- (v) 3,5-Dinitrosalicylic acid(DNSA)
- (vi) 3,5-Dibromosalicylic acid(DBSA)
- (vii) 1-Hydroxy-2-naphthoic acid(HNA)
- (viii) Iminodiacetic acid and(IMDA)
- (ix) Pyridine-2, 6-dicarboxylic acid (PDA).



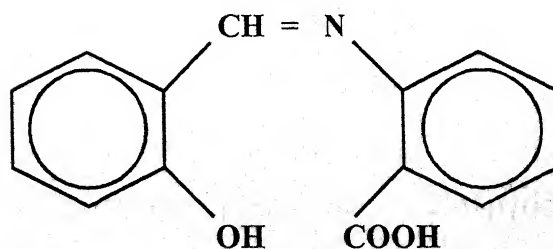
(a) 2,2' - dithiosalicylic acid (DTSA)



(b) Diphenylamine- 2, 2' - dicarboxylic acid (DPDC)



(c) 2 - hydroxybenzilideneaminothiophenol(HBAT)



(d) 2 - hydroxybenzilideneanthranilic acid (HBAA)

FIGURE 1.1 THE NEW LIGANDS

The ternary 1:1:1 complexes of copper (II), nickel (II) and cobalt (II) were synthesized with 3,3'- bipyridine as well as one ligand for one series each and one of the 13 aforementioned ligands as the other ligand to prepare two series of such ternary complexes with the general formula $M(II)-B-H_2A$ where

$M = Cu(II), Ni(II) \text{ and } Co(II);$

$B = 4,4'$ -dipyridine (dipy.) or 4,7-dimethyl-1, 10-phenanthroline and

$H_2A =$ One of the four synthesized ligand or one of the nine selected for their biological importance.

A list of the mixed ligand complex ligand synthesized is given below:

Copper ternary complexes with (dipy.)

- (i) Thiodipropionato-2, 2'-dipyridinecopper(II) complex or Cu (dipy.) (TDPA)
- (ii) 2-Mercaptobenzoato-2, 2'-dipyridinecopper(II) or Cu (dipy.)(MBA)
- (iii) Thiodiacetato- 2,2'-dipyridinecopper(II) or Cu (dipy.)(TDAA)
- (iv) 2,2'- Dithiosalicylato-2, 2'-dipyridinecopper(II) or Cu (dipy.) (DTSA)
- (v) Dithiopropionato- 2,2'-dipyridinecopper(II) or Cu (dipy.)(DTPA)
- (vi) Pyridine-2, 6-dicarboxylato- 2,2'-dipyridinecopper(II) or Cu (dipy.) (PDA)
- (vii) 2-Hydroxybenzilidine-2-aminothiophenolato- 2,2'-dipyridinecopper (II) or Cu (dipy.)(HBAT)
- (viii) 2-Hydroxybenzilidine-2-aminophenolato-2, 2'-dipyridinecopper(II) or Cu (dipy.) (HBAA)

- (ix) 3,5-Dinitrosalicylato- 2,2'-dipyridinecopper(II) or Cu (dipy.)(DNSA)
- (x) 3,5-Dibromosalicylato-2, 2'-dipyridinecopper(II) or Cu (dipy.) (DBSA)
- (xi) 1-Hydroxy-2-naphtholato- 2,2'-dipyridinecopper(II) or Cu (dipy.) (HNA)
- (xii) Iminodiacetato- 2,2'-dipyridinecopper(II) or Cu (dipy.)(IMDA)
- (xiii) Diphenylamine-2, 2'-dicarboxylato- 2,2'-dipyridinecopper(II) or Cu (dipy.) (DPDC)

Cobalt ternary complexes with (dipy.)

- (i) Thiodipropionato-2, 2'-dipyridinecobalt(II) complex or Co (dipy.) (TDPA)
- (ii) 2-Mercaptobenzoato-2, 2'-dipyridinecobalt (II) or Co (dipy.)(MBA)
- (iii) Thiodiacetato- 2,2'-dipyridinecobalt (II) or Co (dipy.)(TDAA)
- (iv) 2,2'- Dithiosalicylato-2, 2'-dipyridinecobalt (II) or Co (dipy.) (DTSA)
- (v) Dithiopropionato- 2,2'-dipyridinecobalt (II) or Co (dipy.) (DTPA)
- (vi) Pyridine-2, 6-dicarboxylato-2, 2'- dipyridinecobalt (II) or Co (dipy.)(PDA)
- (vii) 2-Hydroxybenzilidine-2- aminothiophenolato- 2,2'-dipyridinecobalt (II) or Co (dipy.)(HBAT)
- (viii) 2-Hydroxybenzilidine-2-aminophenolato-2, 2'-dipyridinecobalt (II) or Co (dipy.) (HBAA)
- (ix) 3,5-dinitrosalicylato- 2,2'-dipyridinecobalt (II) or Co (dipy.)(DNSA)
- (x) 3,5-Dibromosalicylato-2, 2'-dipyridinecobalt (II) or Co (dipy.)(DBSA)

- (xi) 1-Hydroxy-2-naphtholato- 2,2'-dipyridinecobalt (II) or Co (dipy.)
(HNA)

Nickel ternary complexes with (dipy.)

- (i) Thiodipropionato-2, 2'-dipyridine nickel (II) complex or Ni (dipy.)
(TDPA)
- (ii) 2-Mercaptobenzoato-2, 2'-dipyridine nickel (II) or Ni (dipy.) (MBA)
- (iii) Thiodiacetato- 2,2'-dipyridine nickel (II) or Ni (dipy.) (TDAA)
- (iv) 2,2'- Dithiosalicylato-2, 2'-dipyridine nickel (II) or Ni (dipy.) (DTSA)
- (v) Dithiopropionato- 2,2'-dipyridine nickel (II) or Ni (dipy.) (DTPA)
- (vi) Pyridine-2, 6-dicarboxylato-2, 2'- dipyridine nickel (II) or Ni (dipy.)
(PDA)
- (vii) 2-Hydroxybenzilidine-2- aminothiophenolato- 2,2'-dipyridine nickel
(II) or Ni (dipy.) (HBAT)
- (viii) 2-Hydroxybenzilidine-2-aminophenolato-2, 2'-dipyridine nickel (II)
or Ni (dipy.) (HBAA)
- (ix) 3,5-dinitrosalicylato-2, 2'- dipyridine nickel (II) or Ni (dipy.) (DNSA)
- (x) 3,5-Dibromosalicylato-2, 2'-dipyridinenickel (II) or Ni (dipy.) (DBSA)
- (xi) 1-Hydroxy-2-naphtholato- 2,2'-dipyridine nickel (II) or Ni (dipy.)
(HNA)
- (xii) Diphenylamine-2, 2'-dicarboxylato- 2,2'-dipyridine nickel (II) or Ni
(dipy.) (DPDC)

Copper ternary complexes with (phen.)

- (i) 2-Mercaptobenzoato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.) (MBA)
- (ii) 2,2'- Dithiosalicylato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.)(DTSA)
- (iii) Dithiopropionato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.) (DTPA)
- (iv) Pyridine-2,6-dicarboxylato(4,7-dimethyl-1,10-phanathroline) copper (II) or Cu(phen) (PDA)
- (v) 2-Hydroxybenzilidine – 2 - aminothiophenolato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.)(HBAT)
- (vi) 2-Hydroxybenzilidine – 2 - aminophenolato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.) (HBAA)
- (vii) 3,5-Dinitrosalicylato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.)(DNSA)
- (viii) 3,5-Dibromosalicylato (4,7-dimethyl-1, 10-phanathroline) copper (II) or Cu (phen.) (DBSA)

Cobalt ternary complexes with (phen.)

- (i) 2-Mercaptobenzoato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (MBA)
- (ii) 2,2'- Dithiosalicylato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (DTSA)
- (iii) Pyridine-2, 6-dicarboxylato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (PDA)

- (iv) 2-Hydroxybenzilidine – 2 - aminothiophenolato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (HBAT)
- (v) 2-Hydroxybenzilidine – 2 - aminophenolato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (HBAA)
- (vi) 3,5-dinitrosalicylato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (DNSA)
- (vii) 3,5-Dibromosalicylato (4,7-dimethyl-1, 10-phanathroline) cobalt (II) or Co (phen.) (DBSA)

Nickel ternary complexes with (phen.)

- (i) 2-Mercaptobenzoato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (MBA)
- (ii) 2,2'- Dithiosalicylato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (DTSA)
- (iii) Pyridine-2, 6-dicarboxylato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (PDA)
- (iv) 2-Hydroxybenzilidine – 2 - aminothiophenolato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (HBAT)
- (v) 2-Hydroxybenzilidine – 2 - aminophenolato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (HBAA)
- (vi) 3,5-dinitrosalicylato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (DNSA)
- (vii) 3,5-Dibromosalicylato (4,7-dimethyl-1, 10-phanathroline) nickel (II) or Ni (phen.) (DBSA)

The four new ligands and all the ternary complexes so synthesized were subjected to elemental analysis, magnetic measurements, electronic and infra

red spectral studies. Having characterized them, the ternary complexes were studied for their biological activity by observing their biological activity against some microorganisms like fungi and bacteria of the type listed below:

Fungi:

- (i) *Aspergillus flavus*
- (ii) *Aspergillus niger*
- (iii) *Aspergillus fumigatus*
- (iv) *Aspergillus nidulans*
- (v) *Aspergillus sydowii*
- (vi) *Aspergillus terreus*
- (vii) *Aspergillus furasium*

Bacteria:

- (i) *Staphylococcus aureus* (Gram +ve)
- (ii) *Escheichia coli* (Gram -ve)

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CHAPTER - 2

CHAPTER - II

PHYSICOCHEMICAL METHODS

It is widely believed and accepted that stereochemical aspects of metal complexes, whether simple or mixed, can be adequately investigated by combining electronic spectral and infrared spectra data with magnetic measurements. A brief review of the important aspects of the application of three important analytical techniques is presented in the following sections. The measurements are convenient, suitable and sufficient to characterize the molecular structure of ligands and the ternary complexes under investigation.

2.1 Electronic Spectra

Electronic spectra of metal chelates of transition metals can give us an insight into the structure of the complex in terms energy level scheme and chemical bonding. A large number of researcher¹⁻⁵ have studied this type of spectra by concentrating mainly on d-d transitions. The basic feature of splitting of d energy levels in terms of ligand field theory helps us interpret the d-d transition of electrons to our benefit.

There are three regions in the electronic spectra of ligands containing nitrogen, oxygen and sulphur and their corresponding complexes. These are 220-270 nm ($45454-37174\text{ cm}^{-1}$), 270-350 nm ($37174-28571\text{ cm}^{-1}$) and 350-500 nm ($28571-20,000\text{ cm}^{-1}$).

The first two regions contain two main peaks which are attributed to $\pi-\pi^*$ and $n-\pi^*$ transitions linked to nitrogen, oxygen and sulphur functions of the

ligand⁶⁻⁷. The metal to ligand transfer bands and d-d transitions in the crystal field are observed⁸ in the third region.

It is well established that magnitude of d orbital splitting depends upon the surrounding ligand environment. It is also affected by the geometry of the complex. On the basis of electronic spectra data, it has now become possible to discriminate and distinguish four coordinate, whether tetrahedral or square planar, from five coordinate trigonal bipyramidal and six coordinate octahedral geometry of complex.

Square planar geometry of Cu (II) complex^{1,9-14} is hinted at by a broad d-d band in the region of 14000-19000 cm⁻¹. It is representative of the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition. It is to be noted that no d-d transition bands are observed in the region 1000-2000 cm⁻¹ for the tetrahedral complexes of copper (II). But these complexes show a broad asymmetric ligand field band around 13000-17000 cm⁻¹ for ${}^2E_g \rightarrow {}^2T_{2g}$ transition in resembling those in octahedral geometry¹⁵⁻¹⁷. It is possible to account¹⁸ for broadening of the band by Jahn Teller effect. A broad asymmetric band at 12300-14875 cm⁻¹ has also been noticed by Sharma¹⁹ et al. for mixed complexes of Cu (II). As per thier explanation, two degenerate states 2E_g and ${}^2T_{2g}$ are further split into two levels each. As a result ${}^2B_{1g} \rightarrow {}^2A_{1g}$ (ν_1), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_2) and ${}^2B_{1g} \rightarrow {}^2E_g$ (ν) transitions yield bands at 12300-14850, 12500-14850 and 12600-14875 cm⁻¹. However, being so close to each other, the bands tend to coalesce resulting in a broad spectral band. In fact, Srivastava and Saxena¹⁷ were also able to obtain three bands at 13157, 14925 and 25641 cm⁻¹ to account for parallel transitions in the complexes of copper (II).

When 3d non-bonding subshell contains seven electrons as in Co (II), normally tetrahedral or octahedral complexes are expected. However, certain experimental conditions and better ligand positioning may allow Co (II) to exhibit higher coordination number. Thus, three electronic spectral bands in the region of 8000-12000, 13000-16000 and 18000-20000 cm^{-1} are anticipated in the six coordinate Co (III) complexes¹⁸⁻²⁰. These bands correspond to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions respectively. The first transition is weak and is seen as a shoulder. Two intense bands at 15000 and 24000 cm^{-1} for the transition $^4T_{2g}(P) \rightarrow ^4T_{1g}(F)$ and charge transfer respectively are to be seen for polymeric Co (II) complexes in which the metal ion is tetrahedrally coordinated. In $[\text{CuCl}_4]_2^-$ ion, three absorption bands at 5800 cm^{-1} , 15000 cm^{-1} and 17000-23000 cm^{-1} are observed. The third one among these is weaker. These transitions correspond to the $^4A_2(F) \rightarrow ^4T_2(F)$, $^4A_2(F) \rightarrow ^4T_1(F)$ and $^4A_2(F) \rightarrow ^4T_1(P)$ respectively. Similarly several transitions in the region 6000-7000 cm^{-1} , 14000-18000 cm^{-1} and three transitions in the range 8000-11000 cm^{-1} may be expected for Co (II) in the square planar ligand field.

In the case of nickel (II) complexes in octahedral field there are three spin allowed transitions which correspond to $^3A_{2g} \rightarrow ^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow ^3T_{1g}$ (ν_2) and $^3A_{2g} \rightarrow ^3T_{1g}(P)$. It now needs no confirmation that the electronic spectra of low spin Ni (II) complexes is vastly different from those of high spin tetrahedral and octahedral species¹. However, before we discuss the specific cases relating to these transition, shapes of complexes and the observed absorption bands, it would be worthwhile to have an idea of the five parameters which permit the

interpretation of data in different ligand environments. The factors are enumerated below-

- a. Ligand Field splitting factor [$10 Dq$ or Δ].
- b. Racah's interelectronic repulsion parameter (B).
- c. Nephelauxetic ratio β .
- d. Ligand Field Stabilization Energy [LFSE].
- e. Ratio of spin allowed transitions.

2.2 (a) Ligand Field Splitting Factor ($10 Dq$)

When the d energy levels split in a ligand field, the difference between the two split levels t_{2g} and e_g is called the ligand field splitting energy which is referred to as $10 Dq$ or Δ . The $10 Dq$ values of all systems, under investigation, have been computed by equations due Figg²⁰ and Ballhausen²¹.

One can obtain an adequately accurate value of $10 Dq$ for copper (II) complexes by the V. Agarwal's equation²²

$$10 Dq = \nu_3 + \frac{1}{2} \nu_1 - \frac{1}{3} (\nu_3 - \nu_2)$$

However, when one broad spectral band is observed, the ligand field stabilization energy is computed using the following relationship

$$Dq = \frac{1}{2} \text{transition values}$$

On the other hand, the 10 Dq values for Co (II) complexes are conveniently available from the equation³¹

$$10Dq = \nu_2 - \nu_1$$

The energy of the first band corresponds²⁴ to the 10 Dq in the case of Ni (II) complexes in the weak field as by configuration interactions, the second and third transitions become indistinguishable.

2.2 (b) Racah Inter-Electronic Repulsion Parameter

The energy of the terms above the ground term within a configuration may be interpreted by inter-electronic repulsions. These energies are of functions of Racah's parameter represented by the symbol B.

The Racah parameter²⁵ B₀ values²⁸ based on electronic configuration (d²-d⁹) for gaseous ions are listed in table 2.01.

It is possible to calculate the B values for the metal ions under investigation using the relationship²³⁻²⁶

$$B = \frac{\nu_2 + \nu_3 - 3 \nu_1}{15}$$

With the knowledge of calculated or say theoretical value of interelectronic repulsions, parameter B₀, the reduced values of B in complex systems can be obtained²⁷.

TABEL - 2.01

$3d^n$	Ion	RACAH parameter (Bo)
$3d^2$	Ti^{2+}	720
	V^{3+}	860
	Cr^{4+}	1040
$3d^3$	V^{2+}	765
	Cr^{3+}	1030
$3d^4$	Cr^{2+}	830
	Mn^{3+}	1140
$3d^5$	Mn^{2+}	960
$3d^6$	Fe^{2+}	1060
	Co^{3+}	1100
$3d^7$	Co^{2+}	1120
$3d^8$	Ni^{2+}	1080
$3d^9$	Cu^{2+}	1240

2.3 (c) Nephelauxetic Effect

The Russel Saunders (R.S.) states are smaller in coordinated metals compared to the free metals. This difference in the R.S.states is attributed to the repulsions within the d electron cloud on coordination. It may, therefore, be concluded that the charge cloud has dilated leading to decrease in energy separation between the states. Obviously, the mean distance between the d electrons increases. As a result, inter electronic repulsions exhibit a decrease.

This phenomenon is termed as Nephelauxetic Effect. The magnitude of this effect is expressed in terms of nephelauxetic ratio (β) by the relationship

$$\beta = \frac{B(\text{in coordinated ion})}{B_o(\text{in free ion})}$$

In fact, the value of β is a direct measure of covalent character in metal to ligand bond in a complex. If $\beta = 1$, the bond is 100 percent ionic. $\beta = 0.5$ indicates 50 percent covalent character in the metal to ligand bond in the complexes in the studies being undertaken.

2.1(d) Ligand Field Stabilization Energy

When in a Ligand field, the degenerate energy levels are split, the difference in energy of the lowest level among the split-levels and the center of gravity of the system is known as ligand field stabilization energy. It is the usual practice to express the LFSE as gain in energy in terms of unit of Dq . In the case of a weak ligand field, the LFSE for any configuration can be found from the energy of the lowest level.

$$LFSE = \frac{XDq}{350}$$

where X varies with variation in d^n configuration

The LFSE values for various d^n values in tetrahedral and octahedral ligand fields are listed in table 2.02.

TABEL - 2.02

EC	LFSE		
	Weak field (Octahedral)	Wak field (tetrahedral)	Strong field (Octahedral)
d^5	0	0	20 Dq (15 F_2 – 275 Fu)
d^6	4 Dq	6 Dq	24 Dq (5 F_2 + 255 Fu)
d^7	6 Dq	12 Dq	18 Dq (7 F_2 + 105 Fu)
d^8	12 Dq	6Dq	12 Dq
d^9	6 Dq	4Dq	6 Dq
d^{10}	0	0	0

2.2 (e) Ratio Of Transitions (ν_2/ν_1)

The magnitude of the ratio of transitions (ν_2/ν_1) can lead us to the geometry of a complex. Thus, theoretically, the six coordinated regular octahedral complex should have ν_2/ν_1 in the range of 1.8 to 2.2 But for distorted octahedral shape^{1,28} the ratio stands lowered to 1.20-1.74. However, for the four coordinate metal complexes no such ratio has been reported thus far.

2.1 Experimental

For the study of electronic spectra of the ternary complexes presently being reported in the subsequent chapters, Bausch and Lomb Electronic 20 and Backman DU-6 Spectrophotometers were used for all dipy. metal and phenanthroline metal complexes. The solvent used was either DMF or DMSO.

2.3 Infra Red Spectral Studies

Infra red spectroscopy occupies an exalted position among techniques utilized for determination and structure of organic compounds as well as metal coordination compounds. This brand of spectroscopy is helpful in identifying and authenticating the presence of functional groups and assessing the nature of bonding in coordination compounds.

The synthesis and characterization of a number of mixed ligand complexes has been carried out by infrared studies by many investigators²⁹⁻³³. The characterization of inorganic metal complexes can also be carried out; an account which has been presented by Nakamoto³⁴.

A careful review of these reports and the interpretation of vibration frequencies in IR spectroscopy leads to precious information which can be used to identify the functional groups present, assess the type of bonding and establish the ligand chain length in addition to arriving at degree of molecular symmetry and isomerism exhibited by complex molecules. When a ligand forms a complex with a metal, the frequency of its IR vibration is generally lowered.

In totality, the following changes can be observed in the IR spectrum of a ligand when it coordinates with a metal ion to form a complex.

- (i) Change in position of bands
- (ii) Change in relative intensities of bands.
- (iii) Split in IR vibration due to lowering of symmetry as due to coordination, degeneracy of certain levels of the ligand is destroyed.

It may be noted that high frequency vibrations in the range $4000-650\text{ cm}^{-1}$ are ligand sensitive and are due to the presence of the ligand. On the other hand, those of the low frequency in the range $650-50\text{ cm}^{-1}$ are metal sensitive and are due to metal ligand bonding.

Let us have a look at some common characteristics IR bands and frequencies due to ligands and complexes.

Bands in the region of 3100 cm^{-1} and $1660-1590\text{ cm}^{-1}$ (stretching) indicate the presence of C-H and C=C in the ligand respectively. The out of plane deformation of C-H is observed at $990-675\text{ cm}^{-1}$. The carboxylic group and a ring system in a molecule is inferred from IR bands in the region $1750-1600\text{ cm}^{-1}$ and 1200 cm^{-1} , and $1100-1000\text{ cm}^{-1}$ and $900-650\text{ cm}^{-1}$ respectively.

In the free Schiff's bases, the characteristic frequency (ν_0) for OH and azomethine occur at 3500 cm^{-1} and 1660 cm^{-1} respectively. However, on complexation, the ν_{OH} band just disappears due to deprotonation. The frequency of the carboxylic group in such cases, observed at 1645 and 1550 cm^{-1} , shifts to lower regions on complexation. If such is the case, both the groups participate in bond formation with the metal ion.

The $\text{C}\equiv\text{N}$ part in the aliphatic Schiff's bases shows a band around 1670 cm^{-1} . In the aromatic Schiff's bases, however, $\text{C}\equiv\text{N}$ band occurs in the region of 1630 cm^{-1} . The electron density in the $\text{C}\equiv\text{N}$ region decreases if the coordination takes place through imine nitrogen. In that case, for obvious reasons, the $\text{C}\equiv\text{N}$ stretching is greater compared to the uncoordinated Schiff's base.

In case hydrogen bonding is present, the ν_{OH} stretching vibration has the absorption peak around $3520-3500\text{ cm}^{-1}$. There is further shifted to a lower frequency region if the coordination occurs through the hydroxyl group.

In the free ligand, the carboxyl stretching vibration frequency and that of the carboxylic group is of observed in the region of 1680 cm^{-1} . A detectable lowering of this band takes place when the ligand links to the metal ion through carbonyl oxygen and carboxylic oxygen.

A band occurring at 1630 cm^{-1} is assigned to the $C\equiv N$ stretching frequency. This frequency is also lowered when metal forms chelates by coordination through azomethine nitrogen. A band at $\sim 1500 - 1440\text{ cm}^{-1}$ is attributed to the aromatic $C=C$ stretching vibration.

Fujita and coworkers³⁵ studied the IR spectra of some molecules and made some useful observations.

In the region of $900-800\text{ cm}^{-1}$ some bands associated with coordinated water molecules are observed. But the strength of the coordinated bond and extent of hydrogen bonding determines their appearance. One cannot just assign the bonds in the region to coordinated water in all the cases, as there is no possibility of stretching and bending of atoms in the stated region. Perhaps, the observed bonds may be attributed to some kind of wagging, twisting or rocking motion. There are certain definite requirements for the bands to occur in the region. The requirements can be summed up as :

- (a) water molecules linked as ligand and not as water of crystallization.
- (b) adequate strength of the M – O bond.
- (c) sufficiently strong hydrogen bonds formed by ligand water molecules with neighboring atoms.

When coordination takes place through nitrogen atoms of =NH group, there is lowering of ν_{N-H} vibration in the form of a special band in the region of 3400cm^{-1} . This is so in the case of ligands such as IMDA and DPDC.

Free ligands like TDPA and DTPA show bands of moderate intensity in the regions around 2130 and 2850 cm^{-1} . These bands may be attributed to the symmetric and asymmetric $\text{CH}_2\text{-S}$ stretching frequencies respectively. When these ligands form chelate complexes there is a marked shift in these frequencies in the corresponding complexes. The shifts are attributed to the coordination of the ligand to the metal through S atoms of the $\text{CH}_2\text{-S}$ group. Further, a moderate band in the region of $570\text{-}660\text{ cm}^{-1}$ assigned to C-S stretching vibration in the free ligand is also shifted. One can obviously infer the involvement of S when a complex is formed with a metal ion. S-S stretching vibration observed at 500 cm^{-1} in the spectral study of a free ligand also shows a shift clearly attributable to the fact that complexation has taken place involving S to form a metal to sulphur bond.

In this connection Adams³⁶ has reported that the metal-sulphur stretching frequencies lie in the range of $480\text{-}210\text{ cm}^{-1}$. The frequencies Pb-S band and Pt-S band for a number of complexes have been found to lie between $400\text{-}280$

cm^{-1} . It goes without saying that the metal to sulphur bending frequency remains unaffected by the atomic weight of the metal used to form the complex.

The metal-nitrogen bond exhibits a stretching frequency below 200 cm^{-1} . The unidentate amine show it at $500\text{-}300 \text{ cm}^{-1}$ while for pyridine complexes it lies between $287\text{-}200 \text{ cm}^{-1}$. The tetragonal diamine complexes of Co (II) and Ni (II), Lever has shown³⁷, have $\nu_{\text{M-N}}$ in the range of $400\text{-}338 \text{ cm}^{-1}$. Justifiably, it is not easy to characterize the M-N linkage with a great degree of certainty in metal chelates. However, Livingstone and Nolan³⁸ have found that $\nu_{\text{M-N}}$ and $\nu_{\text{M-S}}$ in Ni (II) complexes of tridentate ligands appear at $415\text{-}412 \text{ cm}^{-1}$ and $328\text{-}326 \text{ cm}^{-1}$ respectively in Ni (II) complexes of tridentate ligands.

2.32 Experimental

A Perkin-Elmer Spectrophotometer (model 521) installed at the Instrumentation Center at IIT, Delhi was used to carry out I R spectral studies of synthesized ligands and ternary complexes in the frequency range of $4000\text{-}200 \text{ cm}^{-1}$ at the room temperature. The pellets of the compounds were made by grounding them thoroughly with Csl.

3.4 Magnetic Studies

3.41 Introduction

In the arriving at the stereochemistry of complex molecules, the knowledge of their magnetic moment can play an important role. The ligands present around the metal ion affect the arrangement and distribution of electrons in the d orbital. Therefore its (magnetic moment) knowledge serves as a tool to

establish the type of bond between metal and atom at the coordinating site, oxidation state of the metal and also the stereochemistry of the complex, as we shall describe in the following lines.

The electrical nature of atom and the energy state of the relevant atom or molecule are the cause of presence of magnetic susceptibility in any species. As we know, the distribution of electrons in d orbitals of a metal depend upon the arrangements of ligands surrounding it. A number of aspects of factors affecting magnetic susceptibility were taken up by Kolam³⁹.

Earlier, pioneering work done by Pauling on application of magnetic measurements on study of complex has laid down the framework for further investigations in the field. Even today, it is the basis of any research of related problems. An advance towards explaining the often large difference of magnetic moment the first, second and third row transition elements of the same configuration and its temperature dependence was made by Kolam by including spin orbital coupling effect into strong field coupling effect. Consequently, it has been possible to rationalize the abnormal behavior of the transition metal complexes. The following factors are considered vital for the purpose.

- (i) increase in spin orbital coupling χ of the metal.
- (ii) greater separation between t_{2g} and E_g orbitals due to greater crystal field repulsions
- (iii) predominance of intermediate forms of complexes over Russel Saunder's coupling complain.
- (iv) the effect of ferromagnetic anti ferromagnetic interaction

9 electrons are present in the third sub shell of copper (II) i.e. there is one unpaired electron obviously, its compounds should have a magnetic moment of 1.73 BM whatever type of bond it forms. However, the copper (II) complexes involving strong ionic/ weak covalent bond possess a magnetic moment in the range of 1.9 to 2.2 BM and for strong covalent /weak ionic bond in the range of 1.72-1.82 BM it may be inferred that copper (II) compounds with sub normal magnetic moment greater than 1.73 BM are distinctly characterized by a weak covalent bond. Most of such complexes are dimeric with two copper (II) ions in the molecules. So almost all such compounds have magnetic coupling as inferred by a number of researches.⁴⁹⁻⁹⁸ Thus, like copper (II) acetate monohydrate such complexes are binuclear.

The overlapping of all orbitals is also able to account for the subnormal magnetic moments of Cu (II) complexes. The magnetic moment is affected by extent of overlap d orbitals. Larger overlap of d orbitals results in larger interaction between Cu (II) – Cu (II) ions. The distance between the two ions also affects the extent of this overlap.

It has been established that the magnetic moment value of Cu (II) carboxylate increases with increase in electron withdrawing ability of the carboxylate ligand. As a result there is lesser Cu (II) – Cu(II) interaction the increase in coordinating ability of trans – axial ligand⁴⁹ also increases the magnetic moment of complexes. As already stated, theoretically, whatever the geometry, the Cu (II) complexes are expected to possess a magnetic moment of 1.70 BM corresponding to the presence of one unpaired electron. If the value of magnetic moment approaches this value, the must be monomeric in nature.

Bicket ⁵⁰ has reported that in square planar, tetrahedral and distorted octahedral Cu(II) complexes, the room temperature magnetic moment falls in the range of 1.85 – 1.86, 1.90 – 2.00 and 1.90 – 1.93 B.M. respectively.

It has been shown⁵¹ on the basis of magnetic measurements that the metal ion in Co (II) complexes has a tendency to increase its coordination number from 4 to 6 without breaking the chelate ring. The paramagnetic behavior of Co (II) complexes can also be explained on the basis of magnetic measurement. The Co (II) ion with a configuration of d^9 can undergo sp^3d^2/d^2sp^3 , or dsp^2 hybridization to form octahedral, tetrahedral and square planar complexes respectively. The square planar complexes of Co (II) are paramagnetic corresponding to one unpaired electron; octahedral or tetrahedral complexes possess magnetic moment corresponding to three unpaired electrons. The square planar complexes of Co (II) have magnetic moment of 2.1 to 2.8 BM in the octahedral geometry the magnetic moment is found to be in the range of 4.7 to 5.2 BM corresponding to three unpaired electrons. The magnetic moment in tetrahedral Co (II) complexes should have spin only value of 3.8 if there is electron pairing between the metal ion and the ligand. It also corresponds to three unpaired electrons.

For octahedral Co (II) complexes, orbital contribution would be small with negligible electron pairing. However in the case of square planar complexes the orbital contribution is large. As per Figgis and Nyholm⁵²⁻⁵³ this difference is helpful and in deciding the stereochemistry of a complex. The reverse situation prevails when there is electron sharing in square planar complexes of Co(II).

Many references are available on magnetic moment of octahedral and square planar complexes of Ni (II) including their temperature dependence and crystal anisotropy. It has been experimentally verified that tetrahedral and octahedral nickel (II) complexes have their effective magnetic moment values in the range of 3.40 – 4.20 BM and 2 and 3 – 3.40 BM. Distortion of octahedral shape increases the magnetic moment. From the point of view of magnetic properties, it is useful to divide Ni (II) complexes into three classes:

- (i) six coordinate octahedral paramagnetic complexes in the $^3A_{2g}$ ground term (magnetic moment bet 2.0 – 3.3 BM)
- (ii) four coordinate tetrahedral paramagnetic complexes with $^3T_{1g}$ ground term (magnetic moment range 3.2-4.0 BM and
- (iii) four coordinate square planar diamagnetic complexes with singlet ground term.

Since the contribution of magnetic moment depends upon electronegativity of attached ligand and is very sensitive to slight departure from cubic symmetry of octahedral complexes, it is not quite satisfactory to distinguish between octahedral and tetrahedral symmetry in the case of Ni (II) and Co (II) complexes⁵⁷.

4.2 Experimental

Generally, one of the following three methods may be applied to determine the magnetic susceptibility of the complexes

- (i) NMR method
- (ii) Faraday's method
- (iii) Gouy's method⁵⁸⁻⁶¹

However, Gouy's method being simple and easily affordable has been used in our present investigations.

GOUY'S METHOD

All the measurements were carried out at the room temperature in the magnetic field of 5kg and 10 kg. The tube constant was determined using AR (BDH) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($g = 5.8472 \times 10^{-6}$ CGS units at 20°C) as the calibrant. Finally powdered sample was filled up to a fixed mark in a hard glass specially designed tube. The specimen tube was suspended in one pan using a silver string in a closed glass chamber to avoid any air damping. Magnetic field from 5×10^3 to 10×10^3 Gauss was generated by an electromagnetic field from a controlled A.C. mains pure supply.

The following data was used to compute the magnetic susceptibility of the complexes being investigated.

- (i) Weight of empty glass tube without magnetic field = W_1g
- (ii) Weight of empty glass tube without magnetic field = W_2g
- (iii) Glass tube + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ without magnetic field = W_3g
- (iv) Glass tube + $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with magnetic field = W_4g

ΔW , the change in weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is given by

$$\Delta W = (W_4 - W_3) - (W_2 - W_1)$$

The total magnetic force (F_0) on a tube containing $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or any substance is given by

$$F = \frac{1}{2} A.K.(H^2 - H_o^2) \quad 1$$

Where

A = area of cross section of the glass tube.

B = susceptibility constant

H = the field in center of pole gap of a magnet

H_o = the field in region out of influence of the magnet

But since $H \gg H_o$, H_o is negligible

$$F = \frac{1}{2} A.K.H^2 \quad 2$$

But $F = g. \Delta W$

$$\therefore \frac{1}{2} A.K.H^2 = g. \Delta W \quad 3$$

$$i.e. \quad K = \frac{2g. \Delta W}{\Delta H^2} \quad 4$$

The value of specific susceptibility is given by

$$\chi = \frac{K}{P} \quad 5$$

where d is density

$$\therefore \chi = \frac{2g}{H^2} \times \frac{AW}{A} \times \frac{1}{P} \quad 6$$

$$But \quad P = \frac{W}{V}$$

Using Pascal's constant, diamagnetic correction is applied and corrected molar magnetic susceptibility values are obtained as per expression

$$\chi'_m = \chi_m - (\text{diamagnetic correction})$$

The effective magnetic moment (μ_{eff}) is given by the following expression

$$\mu_{\text{eff}} = 2.84 \chi'_m \cdot T$$

Where T is the absolute temperature

From μ_{eff} , the number n of unpaired electrons can be computed using the relation

$$\mu_{\text{eff}} = n(n+2)$$

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CHAPTER - 3

CHAPTER - III

SYNTHESIS ELEMENTAL ANALYSIS AND MICROBIAL STUDIES

Introduction

As indicated in chapter 1, four novel ligands were synthesized and their elemental analysis was carried out, nine others were used to prepare complexes with Ni (II), Cu (II) and Co (II) with 3,3'- dipyridine and 4, 7, - dimethyl -1, 10 phenanthroline which were then subjected to elemental analysis. The following lines describe the nature of reagents used and the procedures followed for the syntheses, elemental analysis and microbial studies.

3.1 Synthesis of ligands

All the reagents used were of analytical purity grade. The four new ligands were synthesized by following the usual practice of preparing azomethines by the condensation of a primary amine with an active carbon. It is known¹ that Schiff's bases are formed via carbinolamine as intermediate, which, on loss of a water molecule, yield the desired base. The process for the synthesis of the four ligands is described in the following sub-sections.

3.1.1 Synthesis of 2 - hydroxy benzalidine anthranilic and (HBAA)

6.9 g (0.05 mole) of anthranilic acid was dissolved in minimum amount of ethanol and mixed with a 5.32 ml (0.05mole) of salicylaldehyde in 25 ml

ethanolic solution. The mixed solution was refluxed over a water bath for one hour. It was allowed to stand overnight. Orange red crystals were obtained. The crystals were filtered off and washed with water several times. After final washing with ethanol, the crystals were dried.

3.1.2 Synthesis of 2- hydroxybenzalidine – 2 –amino phenol (HBAT)

Ethanolic solution of (0.05 mole) of aminophenol in ethanol and (.05 mole) of anthranilic acid also in ethanol were mixed together, and refluxed on a water bath for over one hour. Dark yellow crystals so obtained were filtered and washed with alcohol and some ether. They were finally recrystallised from ethanol.

3.1.3 Synthesis of diphenylamine –2, 2- dicarboxylic acid (DPDA)

0.05 mole of each anthranilic and o-chlorobenzoic acid respectively were taken in a flask fitted with a condenser. Water was added to make the solution aqueous and the solution was neutralized with potassium carbonate. The mixture so obtained was refluxed on a water bath for about five hours. Animal charcoal was added to decolorize the solution and the contents boiled and filtered under suction. The filtrate was acidified with dilute hydrochloric acid and then allowed to cool. A solid was precipitated. It was filtered, washed and recrystallised from alcohol.

3.1.4 Synthesis of 2,2'- dithiosalicylic acid (DTSA)

10g of thiosalicylic acid was suspended in water and reacted with 2g of copper sulphate solution acidified with 2 ml of 4 N hydrochloric acid while stirring the mixture for about an hour gave a crystalline precipitate. After filtration, the crystals were recrystallised from 95% acetone.

3.2 Synthesis of ternary complexes

The complexes were synthesized by the method due to Walton et al.^{2,3} and Musumeci et al.^{4,7} Thus, one of the following two procedures was followed for the purpose. For purposes of calculation of 2×10^{-3} moles of ligands, metal salts etc., the molecular weight of the substance was divided by 5000 and the value taken in grams.

Procedure I

The equimolar ($2 \times 10^{-3}M$) amounts of the two ligands (one acidic and other neutral base) were dissolved separately in aqueous / alcoholic / acetic solutions and were mixed together while stirred briskly. The metal acetate in the same molar proportion ($2 \times 10^{-3}M$) dissolved in ethanol was then added slowly with constant stirring and shaking. One was careful to maintain the pH between 5 and 6 by addition of alcoholic ammonia solution.

The mixed well stirred solution was heated on a water bath for about an hour and then cooled. A precipitate separated, the solution was filtered and the precipitate washed with distilled water / benzene / acetone / ether and dried in a vacuum desiccator over fused $CaCl_2 / P_4O_{10}$.

Procedure II

A solution of the acid was prepared in ethanol and mixed with an aqueous solution of metal acetate in the pre-determined proportion to get a metal (II) dicarboxylate solution. It was subjected to evaporation until minute crystals separated. After washing the crystals with a mixture of 50% ethanol – diethylether, they were dried in vacuum over anhydrous aluminum chloride at the room temperature.

The aqueous acetic solution of the simple complex (metal (II) – dicarboxylate) was added to the equimolar solution of the other ligand i.e. the base in alcohol. The complex was precipitated. It was washed with a 50% solution of acetone in water, benzene and acetone in the order stated and then dried at the room temperature under reduced pressure.

3.2.01 Synthesis of M (dipy.) TDPA complexes

A solution of 0.0122g dipyrindine in 25 ml ethanol was added to 25 ml g ethanolic solution of 0.3564 g TDPA with brisk stirring. Procedure I was followed. To this solution an alcoholic solution of metal acetate [0.3993g of Cu (II) acetate monohydrate / 0.4980 g of Co (II) acetate tetrahydrate or 0.4976 g Ni (II) acetate tetrahydrate was slowly added attended by constant stirring by means of a magnetic stirrer. The precipitate was digested over a water bath, filtered under suction and washed with water, acetone, benzene alcohol and ether in the order stated. It was finally dried in vacuum over P_4O_{10} .

3.2.02 Synthesis of M (dipy) HBAA complexes

Procedure I was found suitable for the preparation of this complex. 0.3122g of 3,3'-dipyridine in alcohol, 0.4820g of HBAA also in alcoholic solution and equimolar anions ($2 \times 10^{-3} \text{M}$) of the metal acetate were mixed together accompanied by constant stirring. The pH of the solution was maintained between 5.0 and 6.0 by addition of alcoholic ammonia. The precipitate was digested over a water bath, filtered washed with 1:1 water acetone mixture, alcohol, benzene and then with ether. The washed precipitate was dried over P_4O_{10} in vacuum dessicator.

3.2.03 Synthesis M(dipy.) DTSA complexes

0.61 28g of DTSA in 25ml alcohol and 0,3122g of 3,3' – dipyridine also in alcohol were mixed together with constant stirring. Equimolar amounts of respective metal acetate solution with pH in the range of 5.0 to 6.0 was mixed with constant stirring. The precipitate, so obtained was digested on a water bath, filtered and washed with water, acetone, and benzene and then ether. It was dried in a vacuum dessicator at over phosphorus pentoxide.

3.2.04 Synthesis of M(dipy) TDAA complexes

Procedure II was followed in this case. A solution of TDAA (0.3002g) in alcohol was added to equimolar solution ($2 \times 10^{-3} \text{M}$) of 0.3992 g Cu (II) acetate monohydrate / 0.4976g of Ni (II) acetate tetra hydrate / 0.4980 g Co (II) acetate tetra hydrate to get the corresponding metal dicarboxylate. The solution was evaporated to separate the minute crystals. These were filtered, washed with alcohol and ether and dried over P_4O_{10} in a vacuum dessicator. The boiling

suspension of the crystals was mixed with $2 \times 10^{-3} \text{M}$ solution of 3,3'-dipyridine. The precipitate obtained was filtered, washed and dried as usual over P_2O_5 at the room temperature.

3.2.05 Synthesis of M – (dipy) MBA complexes

As per procedure I, 0.3082g of MBA in 25 ml acetone and to 0.5122 of 3,3-dipyridine in 25 ml of ethanol were mixed together with constant stirring keeping the pH in the range of 5.0 – 6.0. An aqueous acetic (1:1) solution ($2.0 \times 10^{-3} \text{M}$) of the corresponding metal acetate hydrate was added while still stirring the solution. The precipitate so obtained was digested in a water bath, filtered, washed with water, acetone benzene alcohol and ether in the stated order and then dried in vacuum over fused CaCl_2 at the room temperature.

3.2.06 Synthesis of M- (dipy) DTPA complexes

Procedure II was found suitable for the preparation of these ternary complexes. 0.3122 g of 3,3'-dipyridine was added to a warm solution of dithiopropionates prepared by mixing equimolar amounts of metal acetate and DTPA in alcohol. The procedure was accompanied by constant stirring. The colored precipitate was washed as usual with water, acetone, alcohol, benzene and then with ether. It was washed under suction over fused calcium chloride in a vacuum dessicator.

3.2.07 Synthesis of M- (dipy.) DNSA complexes

Following procedure I, 0.4920 g of DNSA in ethanol and 0.3122g of dipyridine also in ethanol were mixed together with constant stirring. The pH of

the solutions was maintained in the range of 5.0 and 6.0 by ethanolic ammonia. The corresponding metal (II) acetate solution in ethanol was added slowly with constant stirring. A parrot green Cu (II) complex, dark yellow Co (II) complex and green Ni (II) complex precipitate obtained was washed successively with different solvents and dried under reduced pressure in a vacuum dessicator.

3.2.08 Synthesis Of M- (dipy) DBSA complexes

Here again the procedure I was found advantageous. 0.5918 g of DBSA and 0.3122 g of 3,3'-dipyridine in ethanolic solutions were mixed vigorously with equimolar amount the metal acetate (2×10^{-3}) in ethanol solution. The pH was not allowed go out of 5.0 to 6.0 range. The precipitate was digested on water bath, filtered, washed as usual, with a number of solvents. The greenish yellow [copper ternary complex], yellow [Co (II) ternary complex] and green [Ni (II) ternary complex] was dried under suction over P_4O_{10} in a vacuum dessicator.

3.2.09 Synthesis of M- (dipy) (HNA) complexes

0.3762 of HNA dissolved in minimum volume of acetone was mixed with 0.3122 g 3,3'-dipyridine in alcohol. The pH was brought in the range of 5.0 and 6.0 and 2×10^{-3} M of the metal was added. Coloured precipitate obtained was digested on a water bath, filtered, washed with water, acetone, benzene and finally with ether. The crystals were then dried at the room temperature under reduced pressure in a vacuum dessicator over P_4O_{10} .

3.2.10 Synthesis of M-(dipy) DPDC complexes

Following procedure II, 0.5140 g of DPDC in alcohol 0.3992 g of Cu (II) acetate monohydrate / 0.4976 g Ni (II) acetate monohydrate also in alcohol were

mixed together, heated on a water bath for evaporation. Crystals of metal dicarboxylate separated. To the suspension of dicarboxylate, 2×10^{-3} M solution of 3,3'-dipyridine (0.3122g) in alcohol was added to get the crystalline precipitate. It was filtered, washed successively with water, acetone and ether. It was dried in a vacuum dessicator over P_4O_{10} at the room temperature.

3.2.11 Synthesis of M- (dipy) HBAAT complexes

0.4580 g of HBAAT was dissolved in alcohol and the pH range of the solution was brought in the range of 5 and 6 by adding ethonolic ammonia. To this solution, 2×10^{-3} Moles of the metal acetate as well as 3,3'-dipyridine were added. Brick red / black /dark brown precipitate was obtained respectively the precipitate was filtered and washed with benzene, alcohol and then ether. The precipitate was finally dried in a vacuum dessicator under reduced pressure over P_4O_{10} .

3.2.12 Synthesis of M-(dipy) PDA complexes

2×10^{-3} dicarboxylate of the three metals prepared as per procedure II were separately dissolved in alcohol and treated with 0.3122 g of 3,3'-dipyridine while maintaining the pH in the range of 5 and 6. The solution was washed, stirred and filtered. The filtrate, on evaporation, yielded blue / blue green / pink crystal for Cu (II) /Ni (II) /Co (II) ternary complex respectively. The crystals were washed successively with water, dried under reduced pressure in a vacuum dessicator.

3.2.13 Synthesis of Cu-dipy IMDA complex

Sodium salt of IMDA (0.2662 g), 0.3122 g of 3,3'-dipyridine and 0.3992 g of Cu (II) acetate monohydrate were mixed together in alcohol. Deep blue

crystals were obtained. They were digested on a water bath, filtered, washed with water acetone, benzene and then with ether. The crystals were dried over P_4O_{10} under reduced pressure in a vacuum dessicator.

3.2.14 Synthesis of Copper (Phen) DTPA complex

0.4202 g of DTPA in ethanol, phenanthroline (Phen) in acetone and the resultant solution was mixed with 0.3992 g of (all concentrations 2×10^{-3} m) of Cu (II) acetate monohydrate while keeping the pH between 5.0 and 6.0. A green precipitate was obtained. It was digested on a water bath, cooled, filtered and washed with water, alcohol, acetone, benzene and then ether. It was dried in a vacuum dessicator at the room temperature and reduced pressure over anhydrous $CaCl_2$.

3.2.15 Synthesis of M-(phen) HBAA complexes

Procedure I was followed. 0.4820 g of HBAA in alcohol, 0.4164 g of (phen) in acetone and alcoholic solution of 2.0×10^{-3} mole of metal acetate in alcoholic solution were mixed gradually accompanied by constant stirring while maintaining the pH between 5 and 6. The precipitate, brown in each case, was digested on a water bath, washed, with solvents as in 3.3.14 and finally dried.

3.2.16 Synthesis of M (phen) DTSA complexes

2×10^{-3} moles of DTSA in alcohol and (phen) in acetone were mixed together with constant stirring. Metal acetate (2×10^{-3} moles) in alcohol was added which keeping the pH between 5 and 6. Light green/ violet precipitate obtained

for Cu (II)/ Ni (II) / Co (II) ternary complexes was digested on a water bath, cooled, filtered and washed and dried as in 3.2.14.

3.2.17 Synthesis of M- (phen.) MBA complexes

0.3028 g of MBA, m ethanol and 0.4164 g of 4,7-dimethyl-1, 10-phenanthroline were mixed with constant stirring. Maintaining the pH between 5 and 6, 0.3992 g of Cu (II) acetate monohydrate/0.4980 g of Co (II) acetate monohydrate /0.4976 g of Ni (II) acetate tetrahydrate was added slowly to the mixed ligand solution. A yellow/ dark yellow/ light green precipitate was obtained for Cu (II)/Co (II)/Ni (II) ternary complex. It was digested on a water bath, cooled, filtered, washed with water, alcohol, acetone and then ether. It was dried over anhydrous CaCl_2 in a vacuum dissicator under reduced pressure.

3.2.18 Preparation of M- (phen) DNSA complexes

2×10^{-3} moles of DNSA in alcohol solution and (phen) in acetone solution were mixed together accompanied by constant stirring. The pH was kept between 5 and 6 and equimolar concentration of the corresponding metal acetate was added gradually. The precipitate obtained was digested over a water bath, cooled, filtered and washed and dried as in sub-section 3.2.17.

3.2.19 Preparation for M- (phen.) DBSA complexes

0.4164g of 4,7- dimethyl-1, 10- phenanthroline (phen) in acetone and equimolar amount of 3,5- dibromosalicylic acid (DBSA) in alcohol were mixed together gradually accompanied by constant stirring. Alcohol i.e. ammonia was added to maintain pH between 5 and 6 and on ethanolic solution of 2.0×10^{-3}

moles of the metal acetate was added again with constant stirring. Light green/pink/green crystalline precipitate was obtained for Cu (II)/ Co (II)/ Ni (II)/ ternary complex. The precipitate was digested washed and dried as sub-section 3.2.17.

3.2.20 Synthesis of M-(phen) HBAT complexes

Procedure II was followed. 0.002 moles of HBAT and equimolar amount of metal acetate were mixed in minimum volume of ethanol. The solution was stirred vigorously and cooled in a water bath. The crystals of metal HBAT salt were obtained. The crystals were separated, dissolved in alcohol and 0.002 moles (0.4164 g) of (phen) in ethanol was added with constant stirring.

The precipitate obtained was digested over a water bath, cooled, filtered and washed with water, alcohol and then ether. It was dried over P_4O_{10} in a vacuum dessicator.

3.2.21 Synthesis of M- PDA complexes

Procedure II was followed and 0.002 moles of metal acetate and PDA were dissolved in ethanol separately. The solutions of (phen) and PDA were mixed and stirred thoroughly keeping the pH of the ligand mixture solution between 5 and 6. The metal acetate solution was added with constant stirring. Blue/Pink/ light green precipitate was obtained for Cu (II)/ Co (II)/ Ni (II) ternary complex. The precipitate was digested on a water bath cooled, filtered, washed with water alcohol, acetone and ether in succession and dried as in earlier sub-sections

3.3 Elemental analysis and molecular formula

The purity of the ligands synthesized and the ternary of the complexes of Cu (II), Ni (II) and Co (II) established by TLC and chemical analysis. The molecular formula, in each case, was derived from elemental analysis, TGA and molecular weight determination. The samples were analyzed for C, H, and N by micro analytical technique at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow, Department of Chemistry, IIT New Delhi and NPL, New Delhi. Tredwells standard method was used for determination of sulphur content in ligands and complexes. Cu (II), Ni (II) and Co (II) content of the complex was determined by gravimetric method as cuprous thiocyanate, Ni-dimethyl glyoximate and Co-dithiocyanate respectively as described by Vogel⁹ in his authoritative texts.

The molecular weights of ternary metal complexes were determined by Rast method and cryoscopic method in DMSO using the following relationship:

$$M = \frac{100 \times W_2 \times K_f}{W_1 \times \Delta T}$$

Where

M = Molecular weight of the compound

W_1 = Weight of the solvent

W_2 = Weight of the compound (solute) whose M is to be found out.

ΔT = Depression in freezing point (in °K)

K_f = Molal depression constant for DMSO = 4.07

The results of elemental analysis legends have been presented in table 3.01 while their physical measurements appear in table 3.02.

Table 3.03 – 3.08 carry the data obtained for ternary complexes of Cu (II), Co(II) and Ni (II). The conductivity measurement, in each case, was carried out on a **Toshniwal** digital conductivity meter (L01.10A) with a dip type cell at $29 \pm 20^\circ\text{C}$ in 10^{-3} M solution of DMF on DMSA.

3.5 Microbial studies

3.5.1 Introduction

The action of organic compounds used as ligands and their ternary complexes with Cu (II), Co (II) and Ni (II) has been investigated.

In terms of microbial studies, any substances capable of arresting the multiplication of pathogens are called 'static' while those capable of killing them are called 'cidal'. In fact, in general, most if not all, 'static' substances' become 'cidal' if concentration and/or time of exposure to substance is enhanced.

On the formation of neutral complexes such as those prepared during the present investigations, the microbial activity of the ligand appears to register an increase probably due to the greater liposolubility of the complex. Presumably, the presence of metal ion facilitates the migration of ligand across the cell membranes. If not, the metal itself must possess toxic characteristics. In the latter case, the coordinated ligand acts as a carrier across the membranes.

A number of chelates ¹⁰⁻¹⁴ of metals such as copper, cobalt, nickel, iron, manganese, magnesium, zinc and gold are found in the biological systems. N,

TABLE – 3.01

ELEMENT ANALYSIS RESULTS OF SYNTHESIZED ORGANIC LIGANDS.

Ligand	% Analysis founds /(Calculated)			
	C	H	N	S
HBAA	78.03 / (77.36)	5.15 / (5.12)	6.59 / (6.26)	11.83 / (11.05)
HBAT	67.01 / (68.12)	5.02 / (4.85)	6.75 / (6.11)	13.90 / (14.00)
DPDC	64.78 / (65.37)	4.10 / (4.32)	5.15 / (5.45)	-
DTSA	55.09 / (54.84)	3.82 / (3.30)	-	21.08 / (20.93)

TABLE – 3.02

PHYSICAL MEASUREMENTS OF SYNTHESIZED ORGANIC LIGANDS.

Ligand	Colour	Melting Point °C	Soluble in formula	Molecular	Molecular Weight Found (Calculated)
HBAA	Orange-red	196°C	Et & DMF	C ₁₄ H ₁₁ NO ₃	225 / (217)
HBAT	Dark yellow	135°C	Ac, M, Et & DMF	C ₁₃ H ₁₁ NSO	235 / (229)
DPDC	White	148°C	A, Ac, Et & Gl	C ₁₄ H ₁₁ NO ₄	253 / (257)
DTSA	White	287°C	M, Et, Ac, Gl, DMF & DMSO	C ₁₄ H ₁₀ N ₃ O ₄	310 / (306)

(Et- Ethanol, Ac – Acetone, Et– Ether, Gl – propylene glycol, M – Methanol, DMF – dimethyl formamide, DMSO – Dimethyl sulphoxide)

TABLE - 3.03

ELEMENTAL ANALYSIS OF COPPER (II) COMPLEXES

Compounds	C	H	N	S	Cu
Cu (dipy.) TDP A.H ₂ O	46.49 / (46.39)	4.35 / (4.39)	6.92 / (6.78)	7.92 / (7.75)	15.25 / (15.35)
Cu (dipy.) MBA	54.98 / (54.87)	3.23 / (3.25)	7.60 / (7.55)	8.71 / (8.62)	16.98 / (17.09)
Cu (dipy.) TDAA.H ₂ O	43.64 / (43.54)	3.63 / (3.67)	7.37 / (5.36)	8.40 / (8.31)	16.36 / (16.47)
Cu (dipy.) DTSA	55.06 / (54.97)	3.05 / (3.08)	5.42 / (6.56)	12.01 / (12.24)	12.04 / (12.13)
Cu (dipy.) DTPA	44.96 / (44.87)	3.74 / (3.78)	6.67 / (10.45)	15.06 / (14.99)	14.75 / (14.85)
Cu (dipy.) PDA.H ₂ O	50.74 / (50.65)	3.23 / (3.26)	10.80 / (8.83)	-	15.67 / (15.78)
Cu (dipy.) HBAA.H ₂ O	60.50 / (60.40)	3.99 / (4.02)	8.92 / (9.04)	-	13.23 / (13.32)
Cu (dipy.) HBAT.H ₂ O	59.48 / (59.38)	4.09 / (4.13)	8.97 / (12.59)	6.89 / (6.90)	13.57 / (13.67)
Cu (dipy.) DNSA	45.65 / (59.38)	2.21 / (2.27)	12.40 / (5.47)	-	14.29 / (14.25)
Cu (dipy.) DBSA	39.81 / (39.73)	2.01 / (1.97)	5.63 / (6.92)	-	12.28 / (12.37)
Cu (dipy.) HNA	62.01 / (62.11)	3.52 / (3.48)	7.02 / (11.39)	-	15.75 / (15.66)
Cu (dipy.) IMDA.H ₂ O	45.43 / (45.57)	4.07 / (4.11)	11.41 / (8.52)	-	17.11 / (17.23)
Cu (dipy.) DPDC.H ₂ O	58.53 / (58.45)	3.86 / (3.89)	8.62 / (6.62)	-	12.93 / (12.90)
Cu (phen.) MBA	59.53 / (59.46)	3.75 / (3.81)	6.72 / (4.87)	7.42 / (7.56)	15.02 / (14.90)
Cu (phen.) DTSA	58.42 / (58.34)	3.42 / (3.51)	5.01 / (5.85)	11.18 / (11.13)	10.92 / (11.03)
Cu (phen.) DTPA	49.92 / (50.00)	4.10 / (4.21)	5.92 / (9.26)	13.21 / (13.36)	13.30 / (13.24)
Cu (phen.) PDA.H ₂ O	55.30 / (55.41)	3.81 / (3.78)	9.20 / (7.96)	-	14.01 / (13.97)
Cu (phen.) HBAA.H ₂ O	63.51 / (63.53)	4.25 / (4.39)	8.04 / (10.60)	-	11.99 / (12.01)
Cu (phen.) HBAT.H ₂ O	51.20 / (51.39)	5.92 / (5.85)	10.52 / (11.28)	8.14 / (8.08)	15.92 / (16.01)
Cu (phen.) DNSA	50.51 / (50.62)	2.92 / (2.84)	11.19 / (4.96)	-	12.69 / (12.76)
Cu (phen.) DBSA	44.42 / (44.56)	2.39 / (2.50)	4.87 / (8.52)	-	11.19 / (11.23)

TABLE - 3.04

PHYSICAL MEASUREMENTS OF COPPER (II) COMPLEXES.

Compounds	Colour	Decomp sition Temp. (°C)	Solution in	Molar Conductance ($\text{Ohm}^{-1} \text{Cm}^2 \text{mol}^{-1}$)	Molecular Formula	Molecular weight Found / (Calculated)
Cu (dipy.) TDDPA.H ₂ O	Blue	206	GI, DMF & DMSO	18.55	Cu (C ₁₆ H ₁₈ O ₅ N ₂ S)	403 / (414)
Cu (dipy.) MBA	Grey	345	M & DMF	18.89	Cu (C ₁₇ H ₁₂ O ₂ N ₂ S)	387 / (372)
Cu (dipy.) TDAA.H ₂ O	Light green	210	M, GI, DMF & DMSO	13.45	Cu (C ₂₄ H ₁₄ O ₅ N ₂ S)	398 / (386)
Cu (dipy.) DTSA	Green	289	GI, DMF 7 DMSO	17.72	Cu (C ₁₆ H ₁₆ O ₄ N ₂ S ₂)	512 / (524)
Cu (dipy.) DTPA	Light blue	205	M, GI, DMF & DMSO	18.38	Cu (C ₁₇ H ₁₆ O ₄ N ₂ S ₂)	420 / (428)
Cu (dipy.) PDA.H ₂ O	Blue	260	M, GI, DMF & DMSO	18.80	Cu (C ₁₇ H ₁₃ O ₅ N ₃)	421 / (403)
Cu (dipy.) HBAA.H ₂ O	Light green	321	DMF & DMSO	19.31	Cu (C ₂₄ H ₁₉ O ₄ N ₃)	489 / (477)
Cu (dipy.) HBAT.H ₂ O	Brick red	271	M, GI, DMF & DMSO	11.62	Cu (C ₂₃ H ₁₉ O ₂ N ₃ S)	452 / (465)
Cu (dipy.) DNSA	Parrot green	269	M, GI, DMF & DMSO	20.10	Cu (C ₁₇ H ₁₀ O ₇ N ₄)	451 / (446)
Cu (dipy.) DBSA	Greenish yellow	249	M, GI, DMF & DMSO	12.10	Cu (C ₁₇ H ₁₀ O ₃ N ₂ Br ₂)	520 / (514)
Cu (dipy.) HNA	Brown	197	M, GI, DMF & DMSO	19.64	Cu (C ₂₁ H ₁₄ O ₃ N ₂)	394 / (406)
Cu (dipy.) IMDA.H ₂ O	Indigo blue	189	M, DMF & DMSO	18.89	Cu (C ₁₄ H ₁₅ O ₅ N ₃)	360 / (396)
Cu (dipy.) DPDC.H ₂ O	Light blue	242	M	19.95	Cu (C ₂₄ H ₁₉ O ₅ N ₃)	478 / (493)
Cu (phen.) MBA	Yellow	214	M, GI, DMF, DMSO & d	7.35	Cu (C ₂₁ H ₁₆ O ₂ N ₂ S)	420 / (424)
Cu (phen.) DTSA	Light gray	258	GI, DMF, DMSO & d	8.89	Cu (C ₂₈ H ₂₀ O ₄ N ₂ S ₂)	567 / (576)
Cu (phen.) DTPA	Green	184	M, GI, DMF, DMSO & d	13.42	Cu (C ₂₀ H ₂₀ O ₄ N ₂ S ₂)	475 / (480)
Cu (phen.) PDA.H ₂ O	Blue	277	M, DMF & DMSO	7.06	Cu (C ₂₁ H ₁₇ O ₅ N ₃)	449 / (455)
Cu (phen.) HBAA.H ₂ O	Dark brown	292	M, GI, DMF, DMSO & d	15.14	Cu (C ₂₈ H ₂₃ O ₄ N ₃)	521 / (529)
Cu (phen.) HBAT.H ₂ O	Brown	233	M, DMF & DMSO	6.14	Cu (C ₂₇ H ₂₃ O ₂ N ₃ S)	389 / (397)
Cu (phen.) DNSA	Parrot green	285	M, DMF, DMSO, d & b	57.00	Cu (C ₂₁ H ₁₄ O ₇ N ₄)	490 / (498)
Cu (phen.) DBSA	Light green	182	M, GI, DMF, DMSO, & d	40.95	Cu (C ₂₁ H ₁₄ O ₃ N ₂ Br ₂)	561 / (565)

TABLE - 3.05

ELEMENTAL ANALYSIS OF COBALT (II) COMPLEXES.

% Analysis Found / (Calculated)

Compounds	C	H	N	S	Co
Co (dipy.) TDPA.H ₂ O	46.80 / (46.92)	4.25 / (4.44)	6.90 / (6.86)	7.68 / (7.83)	14.32 / (14.40)
Co (dipy.) MBA	55.62 / (55.56)	3.27 / (3.30)	7.72 / (7.64)	8.77 / (8.73)	15.92 / (16.05)
Co (dipy.) TDAA.H ₂ O	49.90 / (49.87)	4.32 / (4.20)	6.57 / (6.46)	7.42 / (7.39)	13.53 / (13.61)
Co (dipy.) DTSA	55.42 / (55.46)	3.17 / (3.11)	5.42 / (5.41)	12.25 / (12.35)	11.42 / (11.35)
Co (dipy.) DTPA	45.42 / (45.36)	4.01 / (3.82)	6.58 / (6.63)	15.20 / (15.15)	13.83 / (13.92)
Co (dipy.) PDA.H ₂ O	51.25 / (51.23)	3.27 / (3.30)	10.62 / (10.58)	-	14.69 / (14.80)
Co (dipy.) HBAA.H ₂ O	70.06 / (60.99)	3.99 / (4.06)	8.82 / (8.92)	-	12.58 / (12.48)
Co (dipy.) HBAT.H ₂ O	63.30 / (63.26)	4.45 / (4.54)	8.40 / (8.20)	6.12 / (6.25)	11.47 / (11.51)
Co (dipy.) DNSA	46.14 / (46.26)	2.17 / (2.29)	12.75 / (12.73)	-	13.25 / (13.36)
Co (dipy.) DBSA	40.01 / (40.08)	2.20 / (1.98)	5.48 / (5.52)	-	11.45 / (11.58)
Co (dipy.) HNA	62.69 / (62.82)	3.48 / (3.52)	7.12 / (7.00)	-	14.57 / (14.69)
Co (phen.) HBA.2H ₂ O	59.01 / (60.11)	3.72 / (3.85)	6.90 / (6.70)	7.59 / (7.65)	14.21 / (14.06)
Co (phen.) DTSA	58.86 / (58.81)	3.45 / (3.54)	4.99 / (4.91)	11.10 / (11.12)	10.27 / (10.31)
Co (phen.) PDA.H ₂ O	56.01 / (55.97)	3.78 / (3.85)	9.20 / (9.35)	-	13.00 / (13.09)
Co (phen.) HBAA.H ₂ O	64.00 / (64.09)	4.48 / (3.54)	8.12 / (8.03)	-	11.29 / (11.24)
Co (phen.) HBAT.H ₂ O	51.89 / (52.00)	6.02 / (3.81)	10.75 / (10.73)	8.02 / (8.17)	14.99 / (15.02)
Co (phen.) DNSA.2H ₂ O	51.89 / (51.09)	2.78 / (4.43)	11.45 / (11.38)	-	11.75 / (11.95)
Co (phen.) DBSA.2H ₂ O	44.83 / (44.92)	2.48 / (5.92)	4.91 / (5.00)	-	10.65 / (10.50)

TABLE - 3.06

PHYSICAL MEASUREMENTS OF COBALT (II) COMPLEXES.

Compounds	Colour	Decomposition Temp. (°C)	Solution in	Molar Conductance ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Molecular Formula	Molecular weight Found / (Calculated)
Co (dipy.) TDPA.H ₂ O	Pink	222	D, DMSO & B	5.71	Co (C ₁₆ H ₁₈ O ₅ N ₂ S)	415 / (408)
Co (dipy.) MBA	Light pink	278	DMF, DMSO, m & B	16.22	Co (C ₁₇ H ₁₂ O ₂ N ₂ S)	376 / (367)
Co (dipy.) TDAA.H ₂ O	Pink	195	M, DMF & B	38.63	Co (C ₁₄ H ₁₄ O ₅ N ₂ S)	374 / (380)
Co (dipy.) DTSA	Violet	301	M, DMF, DMSO & B -	4.70	Co (C ₂₄ H ₁₆ O ₄ N ₂ S ₂)	502 / (519)
Co (dipy.) DTPA	Pink	275	DMF & DMSO	38.99	Co (C ₁₆ H ₁₆ O ₄ N ₂ S ₂)	432 / (423)
Co (dipy.) PDA.H ₂ O	Light pink	284	M, Gl, DMF, DMSO & B	13.15	Co (C ₁₇ H ₁₃ O ₅ N ₃)	389 / (398)
Co (dipy.) HBAA.H ₂ O	Light yellow	279	M, Gl, DMF & DMSO	23.58	Co (C ₂₄ H ₁₉ O ₄ N ₃)	465 / (472)
Co (dipy.) HBAT.H ₂ O	Black	291	M, Gl, DMF, DMSO & B	18.60	Co (C ₂₃ H ₁₉ O ₂ N ₃ S)	462 / (458)
Co (dipy.) DNSA	Dark yellow	214	M, Gl, DMF & DMSO	5.10	Co (C ₁₇ H ₁₀ O ₇ N ₄)	451 / (441)
Co (dipy.) DBSA	Yellow	275	M, Gl, DMF & DMSO	17.72	Co (C ₁₇ H ₁₀ O ₃ N ₂ Br ₂)	490 / (509)
Co (dipy.) HNA	Brown	300	Gl, DMF & DMSO	6.20	Co (C ₂₁ H ₁₄ O ₃ N ₂)	405 / (401)
Co (phen.) HBA.2H ₂ O	Dark yellow	305	M, Gl, DMF & DMSO	7.40	Co (C ₁₄ H ₂₀ O ₄ N ₂ S)	440 / (453)
Co (phen.) DTSA	Violet	220	Gl, DMF, DMSO & D	7.60	Co (C ₂₈ H ₂₀ O ₄ N ₂ S ₂)	562 / (571)
Co (phen.) PDA.H ₂ O	Pink	300	Gl, DMF, DMSO & D	9.82	Co (C ₂₁ H ₁₇ O ₅ N ₃)	456 / (450)
Co (phen.) HBAA.H ₂ O	Light yellow	311	M, Gl, DMF, DMSO, D & B	6.67	Co (C ₂₈ H ₂₃ O ₄ N ₃)	514 / (524)
Co (phen.) HBAT.H ₂ O	Dark brown	288	M, Gl, DMF, DMSO, D & B	6.70	Co (C ₂₇ H ₂₃ O ₂ N ₃ S)	381 / (392)
Co (phen.) DNSA.2H ₂ O	Orange	263	M, Gl, DMF, DMSO, D & B	36.48	Co (C ₂₁ H ₁₈ O ₇ N ₄)	516 / (527)
Co (phen.) DBSA.2H ₂ O	Light pink	209	M, Gl, DMF, DMSO, D & B	34.45	Co (C ₂₁ H ₁₈ O ₅ N ₂ Br ₂)	586 / (595)

TABLE - 3.07

ELEMENTAL ANALYSIS OF NICKEL (II) COMPLEXES.

% Analysis : Found / (Calculated)

Compounds	C	H	N	S	Ni
Ni (dipy.) TDPA.H ₂ O	47.12 / (47.00)	4.22 / (4.45)	6.92 / (6.86)	7.62 / (7.85)	14.12 / (14.25)
Ni (dipy.) MBA	55.76 / (55.67)	3.39 / (3.31)	7.52 / (7.66)	8.85 / (8.75)	15.75 / (15.88)
Ni Cu (dipy.) TDAA.H ₂ O	50.01 / (49.96)	4.32 / (4.20)	6.57 / (6.48)	7.34 / (7.40)	13.24 / (13.45)
Ni (dipy.) DTSA	55.42 / (55.54)	3.01 / (3.12)	5.42 / (5.41)	12.27 / (12.37)	11.12 / (11.22)
Ni (dipy.) DTPA	45.34 / (45.44)	3.75 / (3.82)	6.58 / (6.64)	15.01 / (15.18)	13.83 / (13.77)
Ni (dipy.) PDA.H ₂ O	51.39 / (51.33)	3.25 / (3.30)	10.62 / (10.60)	-	14.56 / (14.64)
Ni (dipy.) HBAA.H ₂ O	61.00 / (61.09)	3.99 / (4.07)	8.82 / (8.93)	-	12.23 / (12.34)
Ni (dipy.) HBAT.H ₂ O	63.25 / (63.36)	4.45 / (4.54)	8.40 / (8.21)	6.40 / (6.26)	11.17 / (11.37)
Ni (dipy.) DNSA	46.49 / (46.32)	2.35 / (2.29)	12.75 / (12.75)	-	13.32 / (13.21)
Ni (dipy.) DBSA	40.10 / (40.14)	2.05 / (1.99)	5.48 / (5.52)	-	11.17 / (11.45)
Ni (dipy.) HNA	62.82 / (62.94)	3.43 / (3.53)	7.12 / (7.01)	-	14.35 / (14.53)
Ni (dipy.) DPDC.H ₂ O	62.10 / (62.29)	4.29 / (4.31)	6.90 / (7.79)	-	10.90 / (10.78)
Ni (phen.) HBA	55.32 / (55.45)	4.64 / (4.44)	4.99 / (6.18)	7.01 / (7.05)	13.92 / (14.08)
Ni (phen.) DTSA	58.92 / (58.89)	3.45 / (3.54)	9.20 / (4.92)	11.19 / (11.23)	10.32 / (10.20)
Ni (phen.) PDA.H ₂ O	56.01 / (56.07)	3.92 / (3.82)	8.12 / (9.37)	-	13.01 / (12.94)
Ni (phen.) HBAA.H ₂ O	64.27 / (64.18)	4.60 / (4.44)	10.75 / (8.04)	-	11.01 / (11.11)
Ni (phen.) HBAT.H ₂ O	52.21 / (52.10)	5.79 / (5.93)	11.45 / (10.75)	8.25 / (8.19)	14.78 / (14.86)
Ni (phen.) DNSA	51.07 / (51.17)	2.76 / (2.87)	4.91 / (11.40)	-	11.92 / (11.11)
Ni (phen.) DBSA.2H ₂ O	45.09 / (44.98)	2.47 / (2.52)	5.11 / (5.01)	-	10.23 / (10.38)

TABLE - 3.08

PHYSICAL MEASUREMENTS OF NICKEL (II) COMPLEXES.

Compounds	Colour	Decomposition Temp. (°C)	Solution in	Molar Conductance (Ohm ⁻¹ Cm ² mol ⁻¹)	Molecular Formula	Molecular weight Found / (Calculated)
Ni (dipy.) TDPA.H ₂ O	Sky blue	199	M+B 7 DMF + DMSO	5.71	Ni (C ₁₆ H ₁₈ O ₅ N ₂ S)	412 / (409)
Ni (dipy.) MBA	Grey	245	DMF, m + B	2.93	Ni (C ₁₇ H ₁₂ O ₂ N ₂ S)	362 / (366)
Ni (dipy.) TDAA.H ₂ O	Bluish white	252	M, Gl, DMF, DMSO & D	6.55	Ni (C ₁₄ H ₁₄ O ₅ N ₂ S)	372 / (381)
Ni (dipy.) DTSA	Light blue	190	M & B + m	17.22	Ni (C ₂₄ H ₁₆ O ₄ N ₂ S ₂)	508 / (518)
Ni (dipy.) DTPA	Light blue	217	M, DMF, D & B + m	6.60	Ni (C ₁₆ H ₁₆ O ₄ N ₂ S ₂)	420 / (422)
Ni (dipy.) PDA.H ₂ O	Yellowish-green	295	M, Gl, DMF, DMSO, D&B	12.92	Ni (C ₁₇ H ₁₃ O ₅ N ₃)	387 / (397)
Ni (dipy.) HBAA.H ₂ O	Brown	298	M, Gl, DMF, DMSO & D	6.62	Ni (C ₂₄ H ₁₉ O ₄ N ₃)	467 / (471)
Ni (dipy.) HBAT.H ₂ O	Dark brown	278	M, Gl, DMF, & DMSO	5.74	Ni (C ₂₃ H ₁₉ O ₂ N ₃ S)	456 / (460)
Ni (dipy.) DNSA	Parrot green	257	Gl, DMF, DMSO & D	16.35	Ni (C ₁₇ H ₁₀ O ₇ N ₄)	432 / (440)
Ni (dipy.) DBSA	Green	295	M, Gl, DMF & DMSO	13.01	Ni (C ₁₇ H ₁₀ O ₃ N ₂ Br ₂)	510 / (508)
Ni (dipy.) HNA	Yellowish-green	208	Gl, DMF & DMSO	12.60	Ni (C ₂₁ H ₁₄ O ₃ N ₂)	391 / (400)
Ni (dipy.) DPDC.2H ₂ O	Grey	220	DMF, & D	11.70	Ni (C ₂₄ H ₁₉ O ₅ N ₃)	478 / (488)
Ni (phen.) MBA	Light green	271	M, Gl, DMF, DMSO & D	12.42	Ni (C ₂₈ H ₂₀ O ₄ N ₂ S ₂)	402 / (419)
Ni (phen.) DTSA	Light green	238	M, Gl, DMF, DMSO & D	11.20	Ni (C ₂₈ H ₂₃ O ₄ N ₃)	562 / (570)
Ni (phen.) PDA.H ₂ O	Light green	300	M, Gl, DMF, DMSO D&B	11.10	Ni (C ₂₁ H ₁₆ O ₂ N ₂ S)	432 / (449)
Ni (phen.) HBAA.H ₂ O	Dark brown	242	M, Gl, DMF, DMSO, & D.	6.30	Ni (C ₂₈ H ₂₃ O ₄ N ₃)	511 / (523)
Ni (phen.) HBAT.H ₂ O	Brown	287	M, Gl, DMF, DMSO, D & B	8.86	Ni (C ₂₁ H ₁₄ O ₇ N ₄)	382 / (391)
Ni (phen.) DNSA	Canary-yellow	290	M, Gl, DMF, DMSO & D	47.02	Ni (C ₂₁ H ₁₈ O ₅ N ₂ Br ₂)	479 / (492)
Ni (phen.) DBSA.2H ₂ O	Green	215	M, DMF, & DMSO	33.46	Ni (C ₂₈ H ₂₃ O ₄ N ₃)	590 / (597)

O and S containing metal chelates have been used a bactericide¹⁵ while those of gold with sulpha drugs have been investigated¹⁶ for the same purpose. A number of other studies¹⁷⁻²¹ detail the bacteriocidal and fungicidal properties of certain organic compounds and metal chelates.

Metal complexes of phenanthroline, bipyridine and tetrapyridine have also been investigated²²⁻²⁵ for their biological activity. These complexes exhibit a marked ability to inhibit proliferation of gram +ve and gram -ve bacteria. In these complexes, the ligand are strongly bonded to the metal ions. That means the complex should remain undissociated. Change of metal in the complex cation MB^{n+} where B is a ligand such as bipyridine or tetrapyridine and $M = Fe, Rm$ Os, Co, Zn, In has not effect on its biological activity but if, for example, bipyridine is replaced by ethylenediamine, there is a measurable change in biological action. We might, therefore, surmise that the complex as a whole and not a fragment is participating. Thus, the mode of action must be physical and any chemical change is ruled out.

According to Albert²⁵ the antifungal and antibacterial activity of 8-hydroxyquinoline complexes may be attributed to the presence of coordination centers for metal-ligand chelate linkage.

Metal specific antibacterial and antifungal activity has been supported by a number of workers²⁶⁻²⁹.

The microbial activity of schiff's bases is also well studied³⁰⁻³¹. Similarly, ligands and their complexes have been effective for, anti-carcinogenic, anaesthetic, anti-convulsant, anti-tubercular action³²⁻³⁴ and anti-microbial

properties³⁵⁻³⁶. The greater activity of metal chelates of thiosemicarbazones compared to ligands only has been reported²⁸⁻²⁹.

The rate of penetration of the ligand complexes on the ligand alone to the microbe has been found³⁷ to be directly proportional to the lipid solubility of the former. In addition, it has been postulated³⁵⁻⁴¹ that there is linear relationship between microbial activity and lipophilic character of the biocidal agent.

Mecallan and Wilcoxon⁴¹ and Somers⁴² have studied the fungi- toxicity in vitro of some inorganic ions.

The vapours of elementary sulphur from sulphur chelates has been held responsible for fungicidal action of the latter. The vapours diffuse in to the spores or mycelia of the fungus owing to their solubility in the constituents, probably lipids, of the cells.

The natural course of hydrogenation / dehydrogenation reaction is disturbed due formation of H_2S .

It is this H_2S which affects the spores and vitality of the fungus. Fe, Cu, Mn, and Zn present in enzymes also bind with sulphur. Consequently the metabolism, as a whole, of the fungi is disorganized and affected.

The comparative study of toxicity of Cu-oxine salicylate and substituted salicylate ternary complex has been carried out by Anjaneyuler and coworkers⁴⁴. It has been theorized that the Cu-ternary complex dissociates to a binary copper-oxine complex which exhibits its toxicity towards fungi by combining and blocking metal binding sites in enzymes.

On the other hand, Block⁴⁵ has postulated that the neutral chelates break up to free oxine which attaches to metal prosthetic group of the enzyme.

Studies⁴⁶⁻⁴⁷ have also taken place to investigate the effect of synthesized complex of heterocyclic N and S containing ligands.

The present investigations also cover the study of microbial action of newly synthesized compounds and a number of metal chelates of the aforementioned type on selected bacteria.

Experimental

The nutrient solution at pH between 6.5-7.0 was prepared by dissolving 1.5 g of sodium nitrate, 0.5 g of dipotassium hydrogen phosphate, 0.25 g of potassium chloride and 15 g of sucrose in 500 ml of distilled water. 50 ml this solution was taken in different conical flasks and 0.35 g of agar agar (7%) was added to each one of them. The culture media thus prepared was sterilized for about 15 minutes at 15 lbs pressure and 121°C in an autoclave by moist heat sterilization method⁴⁸.

25 mg of ligand or ternary complex dissolved in propylene glycol or DMF or DMSO formed the test solution.

Screening for BIOCIDAL ACTION

Food poisoned technique i.e. agar diffusion method or serial dilution method was used for the purpose.

5ml of sample solution was thoroughly shaken with warm culture medium at 40 °C to make up the volume to 50 ml. The resultant solution was transferred to two different clean petri-dishes containing a little soil. The petri-dishes were inoculated in an inoculation chamber having ultra violet lamp under aseptic conditions ⁴⁸⁻⁵⁰. Blank observations were made to neglect the effect of environment.

All the petri-dishes were placed in an incubator to 32 °C. A 48-hour period was fixed for observation on growth of bacteria in petri-dishes. This period for fungi was kept at 7 days.

All the substances were screened at 500 ppm concentration for which 25g of the substances was dissolved in 50 ml of the culture medium.

Determination of Minimum Inhibitory Concentration (MIC) values

After establishing the microbial activity of the species at 500 ppm, it was considered worthwhile to study their action at lower concentrations to work out the MIC values.

The procedure is similar to that followed for 500ppm described in the subsection 3.5.3. A stock solution of was prepared by dissolving 50mg of the ligand / chelate in 10ml of propylene glycol or DMF. Test solutions corresponding to 100, 200, 300, 400 ppm were prepared by mixing 1, 2, 3 and 4 ml respectively of the stock solution in hot culture medium at $40 \pm 1^\circ\text{C}$ and the volume made up to 50ml in each case.

The specific fungus or bacteria was introduced by the loop of a platinum wire in the petri-dishes for the above set of concentrations. One was careful to sterilize the platinum loop by heating it in an oxidizing flame before use for inoculation of fungus bacteria. The growth of bacteria and fungus was observed for 48-hours and 7 days respectively. The lowest concentration at which the fungi / bacteria was not detectible was identified.

Fungi and Bacteria tested

The ligand and complexes were subjected to biological activity on the following fungi and bacteria

Fungi: (i) <i>Aspergillus sydowii</i>	Blue
(ii) <i>Aspergillus flavus</i>	Yellow green
(iii) <i>Aspergillus niger</i>	Black
(iv) <i>Aspergillus fumigativ</i>	Dark green
(v) <i>Aspergillus nidulanse</i>	Green reverse violet
(vi) <i>Aspergillus terreus</i>	Brown

Bacteria: (i) <i>Staphylococcus <u>aurous</u></i>	Gram + ve
(ii) <i>Escherichia coli</i>	Gram - ve

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CHAPTER - 4

CHAPTER - IV

TERNARY COMPLEXES OF COPPER (II)

Results and Discussion

4.1 Electronic spectra

From the discussion on electronic spectra in the chapter II it follows that on the basis of splitting of energy levels in a ligand field, it is possible to establish assignment of octahedral, square planar and tetrahedral complexes, which have been synthesized in the present investigations.

The electronic spectral data of ternary complexes of copper (II) is summarized in table 4.01 .

Appearance of a broad asymmetric band is expected for the mixed ligand complexes of Copper (II). In the case of Copper (II) complexes, distortion (Jahn seller) from octahedral symmetry results in further break up of two degenerate states viz ${}^2T_{2g}$ into two components in each case.

Consequently, three spectral bands due to following transition are expected

- (a) ${}^2B_{1g} \longrightarrow {}^2A_{1g} (v_1)$
- (b) ${}^2B_{1g} \longrightarrow {}^1B_{2g} (v_2)$
- (c) ${}^2B_{1g} \longrightarrow {}^1E_g (v_3)$

It has been found that three shoulder bands are discernible in the regions of 11510-12026 cm^{-1} , 17300 – 18540 cm^{-1} and 26960-27410 cm^{-1} for Cu (dipy.) (TDAA), Cu (dipy) (TDAA), Cu (dipy) HBAA, Cu (dipy) (IMDA) and Cu (phen.) (DTPA) corresponding to transition (a), (b) and (c). One may, therefore, conveniently assign distorted octahedral geometry to these complexes. Furthermore, the $10Dq$, B and β values have also been evaluated. The ratio ν_2/ν_1 in the range 1.99 – 1.54 is also in support of distorted copper (II) complexes. The β (nephelauxetic ratio) and $\beta\%$ are also suggestive of strong covalent contribution in the metal to ligand bond.

But increase in energy of ${}^2A_{1g}$ makes it sufficiently close to ${}^2B_{2g}$ and 2E_g states. The result is that the three bands overlap due to small energy gap. The overlapping is observed as a broad symmetrical band.

Such a broad spectral band in the region of 16210-18940 cm^{-1} corresponds to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition is observed in the case of Cu (dipy) MBA, Cu (dipy) DNSA, Cu (dipy) DBSA, Cu (dipy.) HNA, Cu (Phen) MBA Cu (Phen) DNSA and Cu (Phen) DBSA complexes. In fact such a band has already been reported for square planar CuO_2N_2 chromophore, It is, therefore, safe to infer that all these complexes possess square planar geometry.

The remaining mixed complexes with Cu (dipy) and Cu (Phen) exhibit a single electronic spectral band in the lower region of 13980-16020 cm^{-1} due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition. It is clear indication of octahedral geometry of these complexes. The assignment of octahedral shape is supported by the calculated $10Dq$ and LFSE values as given in table 4.01

TABLE - 4.01

ELECTRONIC SPECTRAL DATA, THEIR ASSIGNMENT- AND LIGAND PARAMETERS OF Cu (II) COMPLEXES

Compound	Observed Band Position (cm^{-1})	Assignment	10 Dq. (cm^{-1})	6 Dq. (dm^{-1})	Racah parameter (B)	Reduced % of B $= \frac{B \times 100}{B_0}$ ($B_0=1240$)	Nephel- auxetic Ratio (β) $= \frac{B}{B_0}$	% Covalent Character ($\beta\%$) $= \frac{1-\beta \times 100}{\beta}$	LEFSE $= X \text{ Dq.}$ 350 k cal/mole	v_2 / v_1
Cu (dipy) TDPA.H ₂ O	14430	$^2E_g \rightarrow ^2T_{2g}$	7215	4329	-	-	-	-	12.36	-
Cu (dipy) MBA	16970	$^2B_{1g} \rightarrow ^2A_{1g}$	8485	-	-	-	-	-	12.36	-2
	11600	$^2B_{1g} \rightarrow ^2A_{1g}$ [v_1]								
Cu (dipy) TDPA.H ₂ O	17300	$^2B_{1g} \rightarrow ^2B_{2g}$ [v_2]	18240	10944	660.66	53.28	0.5328	87.68	31.26	1.49
	27410	$^2B_{1g} \rightarrow ^2E_g$ [v_3]								
Cu (dipy) DTSA	15376	$^2E_g \rightarrow ^2T_{2g}$	7688	4613	-	-	-	-	13.18	-
Cu (dipy) DTPA	14110	$^2E_g \rightarrow ^2T_{2g}$	7055	4233	-	-	-	-	12.09	-
Cu (dipy) PDA.H ₂ O	13980	$^2E_g \rightarrow ^2T_{2g}$	6990	4194	-	-	-	-	11.98	-
	11510	$^2B_{1g} \rightarrow ^2A_{1g}$ [v_1]								
Cu (dipy) HBAA.H ₂ O	17300	$^2B_{1g} \rightarrow ^2B_{2g}$ [v_2]	8793	5276	686.00	55.32	0.5532	80.76	15.07	1.51
	27410	$^2B_{1g} \rightarrow ^2E_g$ [v_3]								
Cu (dipy) HBAT.H ₂ O	15988	$^2E_g \rightarrow ^2T_{2g}$	7994	4796	-	-	-	-	13.70	-
Cu (dipy) DNSA	17440	$^2B_{1g} \rightarrow ^2A_{1g}$	8720	-	-	-	-	-	-	-
Cu (dipy) DBSA	18940	$^2B_{1g} \rightarrow ^2A_{1g}$	9470	-	-	-	-	-	-	-
Cu (dipy) HNA	17850	$^2B_{1g} \rightarrow ^2A_{1g}$	9825	-	-	-	-	-	-	-
	11780	$^2B_{1g} \rightarrow ^2A_{1g}$ [v_1]								
Cu (dipy)IMDA.H ₂ O	18010	$^2B_{1g} \rightarrow ^2B_{2g}$ [v_2]	15359	9215	642.00	51.77	0.5177	93.16	26.33	1.52
	26960	$^2B_{1g} \rightarrow ^2E_g$ [v_3]								

Table -4.01 Contd..

Cu (dipy) DPDC.H ₂ O	14560	$^2E_g \rightarrow ^2T_{2g}$		7280	4368	-	-	-	-	12.48	-
Cu (phen) MBA	18336	$^2B_{1g} \rightarrow ^2A_{1g}$		9168	-	-	-	-	-	-	-
Cu (phen) DTSA	16020	$^2E_g \rightarrow ^2T_{2g}$		8010	4806	-	-	-	-	13.73	-
	12026	$^2B_{1g} \rightarrow ^2A_{1g}$	[v ₁]								
Cu (phen) DTPA	18540	$^2B_{1g} \rightarrow ^2B_{2g}$	[v ₂]	9002	5401	644.13	51.94	0.5194	92.52	15.43	1.54
	27200	$^2B_{1g} \rightarrow ^2E_g$	[v ₃]								
Cu (phen) PDA.H ₂ O	14480	$^2E_g \rightarrow ^2T_{2g}$		7240	4344	-	-	-	-	12.41	-
Cu (phen) HBAA.H ₂ O	14358	$^2E_g \rightarrow ^2T_{2g}$		7179	4307	-	-	-	-	12.30	-
Cu (phen) HBAA.H ₂ O	15844	$^2E_g \rightarrow ^2T_{2g}$		7922	4753	-	-	-	-	13.85	-
Cu (phen) DNSA	16210	$^2B_{1g} \rightarrow ^2A_{1g}$		8105	-	-	-	-	-	-	-
Cu (phen) DBSA	17400	$^2B_{1g} \rightarrow ^2A_{1g}$		8700	-	-	-	-	-	-	-

4.2 I.R. Spectra

4.2.1. Ternary complexes (dipy) – Cu

The infrared spectral frequencies and their provisional assignment in ternary complexes of Cu (II) containing 3,3'- dipyridine as one of the ligands are summarized in tables 4.02 to 4.14. A brief comment on some prominent peaks is also included in these tables.

As we discussed in a earlier chapter, noteworthy changes occur in the infra red spectra of a free ligand when it gets linked to a metal by co-ordination or covalent bond formation.

In the HBAA, HBAT, DNSA, DBSA and HNA free ligands, the stretching and bending vibrations of phenolic –OH group are indicated by spectral bands at 3450 cm^{-1} , 3250 cm^{-1} , 3490 cm^{-1} , 3240 cm^{-1} , 3450 cm^{-1} and moderate bands at 1365 cm^{-1} , 1370 cm^{-1} and 1380 cm^{-1} , 1375 cm^{-1} respectively. The respective ternary complex of these ligands with Cu (II) that yield IR spectra in which these bands do not occur. It may safely be concluded that complexation occurs through deprotonation of the phenolic-OH group.

The spectral band due –NH stretching vibration in free IMDA and DPDC is observable at 3400 cm^{-1} . Its shifting to a lower frequency in the ternary complex to 3360 cm^{-1} and 3370 cm^{-1} leads us to the conclusion that coordination to the metal has taken place through N atom of NH. 24)

Further in the free IMDA and DPDC ligands, a moderate band at 1585 cm^{-1} is attributed – N-H bending. In fact, it overlaps with the frequency due to the aromatic ring. However, when they form ternary complexes, as stated, this frequency is lowered. It confirms that nitrogen atom is involved in linkage with Cu (II).

TABLE - 4.02

IR SPECTRAL DATA OF dipy./TDPA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	TDPA	Cu (dipy.)TDPA	Probable assignments
-	-	3440 (Sb)	Coordinated H ₂ O mol.
-	2930 (m)	2920 (m)	Asym. CH ₂ -S Stretching
-	2850 (s)	2825 (m)	Sym. CH ₂ -S Stretching
-	1700 (s)	1660 (Sb)	asym. C=O Stretching.
1600 (s)	-	1335 (m)	C = N Stretching (Py.)
1585 (m)	-	1580 (Sb)	Aromatic C-C multiple band.
-	1440 (S)	1400 (Sb)	Sym. C= O Stretching.
-	1415 (m)	1400 (S)	CH ₂ -S deformation.
1410 (m)	-	-	Aromatic C-C multiple band.
-	1360 (m)	1345 (w)	C = O Stretching.
1320 (w)	-	1310 (m)	C - N Stretching (Py.)
-	1250 (S)	1225 (m)	CH ₂ -S wag.
1170 (w)	-	1160 (w)	Pyridine ring.
-	1050 (w)	1040 (w)	C - O Stretching.
-	920 (m)	-	OH deformation.
-	-	840 (mb)	Coordinated H ₂ O- mol.
810 (S)	810 (w)	820 (S)	Out of plane CH bending.
750 (w)	775 (m)	745 (m)	Out of plane CH bending.
740 (w)	760 (w)	750 (w)	Out of plane Ch bending.
-	-	690 (mb)	Coordinated H ₂ O- mol.
680(w)	660 (S)	650 (S)	Out of plane CH deformation.
610 (wb)	-	615 (w)	Py. Ring deformation.
-	590 (w)	565 (w)	C.S. Stretching.
-	525 (m)	-	COOH wagging mode.
-	-	500 (m)	M - O Stretching.
-	-	410 (w)	M - N Stretching.
-	-	270 (m)	M - S Stretching.

TABLE - 4.03

IR SPECTRAL DATA OF dipy./MBA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	MBA	Cu (dipy.)MBA	Probable assignments
-	2590 (w)	-	S-H Stretching
-	1660 (s)	1620 (s)	Asym. C=O Stretching
1600 (s)	-	1590 (m)	C=N Stretching (Py.)
1585 (m)	1600 (m)	1585 (s)	Aromatic C-C multiple band.
1410 (m)	1460 (m)	1470 (m)	Aromatic C-C multiple band.
-	1440 (m)	1400 (s)	Sum. C=O Stretching
1320 (w)	-	1350 (mb)	C-N Stretching (Py.)
1170 (w)	-	1175 (w)	Pyridine ring.
-	1060 (w)	1065 (w)	Benzene breathing.
-	1050 (m)	1040 (m)	C=O Stretching
-	920 (b)	-	OH deformation.
810 (s)	810 (m)	815 (s)	Out of plane CH bending.
750 (w)	-	755 (wb)	Out of plane CH bending.
740 (w)	740 (ms)	-	Out of plane CH bending.
680 (w)	660 (m)	655 (w)	Out of plane CH bending.
-	680 (m)	-	COOH bending.
610 (wb)	-	-	Pyridine ring deformation.
-	570 (m)	550 (wb)	C-S Stretching
-	515 (w)	-	COOH Wagging mode.
-	-	500 (m)	M-O Stretching.
-	-	450 (m)	M-N Stretching.
-	-	340 (m)	Stretching.

TABLE - 4.04

IR SPECTRAL DATA OF dipy./ TDAA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	TDAA	Cu (dipy.) TDAA	Probable assignments
-	-	3400 (mb)	Cotding H ₂ O mol.
-	2930 (s)	2910 (m)	Asym. (CH ₂ -S) Stretching
-	2850 (s)	2810 (m)	Sym. (CH ₂ -S) Stretching.
-	1660 (s)	1610 (s)	Asym. (C=O) Stretching.
-	1400 (s)	1360 (sb)	Sym. (C=O) Stretching.
1600 (s)	-	-	C=N Stretching (Py.)
1585 (m)	-	1585 (sh)	Aromatic C-C multiple band.
1410 (s)	-	1415 (sh)	Aromatic C-C multiple band.
-	1410 (m)	1380 (m)	CH ₂ -S deformation.
1320 (w)	-	-	C-N Stretching. (Py.)
-	1225 (m)	1205 (m)	CH ₂ -S wagging.
1170(w)	-	1155 (w)	Pyridine ring.
-	-	1030 (m)	C-O Stretching.
-	920 (m)	-	OH- deformation.
-	-	⁺ 850 (wb)	Coordinated H ₂ O mol.
810(s)	865 (m)	830 (s)	Out of plane CH bending.
750(w)	825 (m)	765 (m)	Out of plane CH bending.
740(w)	780 (w)	740 (w)	Out of plane CH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
680(wb)	660 (s)	675 (m)	Out of plane CH deformation.
610(wb)	-	600 (w)	Py. Ring deformation.
-	570 (m)	530 (m)	C-S Stretching.
-	-	500 (m)	M-O Stretching.
-	-	395 (w)	M-N Stretching.
-	-	300 (m)	M-S Stretching.

TABLE - 4.05

IR SPECTRAL DATA OF dipy./DTSA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DTSA	Cu (dipy.)DTSA	Probable assignments
-	1690 (s)	1600 (sb)	Asym. C=C Stretching.
1600 (s)	-	1550 (m)	C=N Stretching (Py.)
1585 (m)	1580 (m)	1580 (sh)	Aromatic C-C multiple band
1410 (s)	1460 (m)	1450 (m)	Aromatic C-C multiple band
-	1415 (s)	1380 (sb)	Sym. C=O Stretching.
-	1360 (w)	1330 (m)	C-O Stretching.
1320 (w)	-	1255 (m)	C-N Stretching.
1170 (s)	-	1160 (sh)	Py. Ring.
-	1100 (w)	1095 (mb)	Benezene breathing.
-	910 (s)	-	OH deformation.
810 (s)	800 (m)	815 (m)	Out of plane CH bending.
750 (w)	740 (s)	750 (s)	Out of plane CH bending.
740 (s)	-	740 (m)	Out of plane CH bending.
-	685 (m)	-	COOH bending.
680 (wb)	655 (m)	675 (m)	Out of plane CH bending.
-	650 (m)	620 (m)	C-S Stretching.
610 (wb)	-	615 (w)	Py. Ring deformation.
-	555 (s)	-	COOH Wagging mode.
-	500 (w)	470 (mb)	S-S Stretching.
-	-	510 (m)	M-O Stretching.
-	-	470 (w)	M-N Stretching.
-	-	340 (m)	M-S Stretching.

TABLE - 4.06

IR SPECTRAL DATA OF dipy./ DTPA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DTPA	Cu (dipy.) DTPA	Probable assignments
-	2930 (s)	2900 (mb)	Asym. CH ₂ -S Stretching
-	2850 (m)	-	Sym. CH ₂ -S Stretching
-	1690 (s)	1640 (sb)	Asym. C=O Stretching
1600 (s)	-	1590 (sh)	C=N Stretching. (Py.)
1585 (m)	-	1585 (w)	Aromatic C-C multiple band.
-	1440 (s)	1410 (sb)	Sym. C=O Stretching.
1410 (s)	-	1415 (s)	Aromatic C-C multiple band.
-	1410 (s)	1380 (sh)	CH ₂ -S Deformation.
1320 (w)	-	1290 (m)	C-N Stretching. (Py.)
1170 (s)	-	1165 (w)	Py. ring.
-	1260 (s)	1240 (w)	CH ₂ -S Wagging.
-	1035 (w)	1050 (m)	C-O Stretching.
-	920 (m)	-	OH deformation.
810 (s)	810 (m)	815 (s)	Out of plane CH bending.
750 (w)	-	-	Out of plane CH bending.
740 (s)	-	745 (wm)	Out of plane CH bending.
680 (wb)	655 (m)	-	Out of plane CH bending.
-	660 (w)	650 (w)	C-S Stretching.
610 (wb)	-	600 (w)	Py. Ring deformation.
-	550 (m)	-	COOH Wagging mode.
-	510 (m)	490 (wb)	S-S Stretching.
-	-	430 (wm)	M-O Stretching.
-	-	390 (m)	M-N Stretching.
-	-	310 (wm)	M-S Stretching.

TABLE - 4.07

IR SPECTRAL DATA OF dipy./PDA LIGANDS AND THEIR COPPER COMPLEX

Wave number (cm ⁻¹)			
Dipy.	PDA	Cu (dipy.) PDA	Probable assignments
-	-	3460 (sb)	Coordinated H ₂ O mol.
-	1700 (s)	1680 (sb)	Asym. C=O Stretching.
1600 (s)	1600 (wm)	1590 (s)	C=N Stretching. (Py.)
1585 (m)	1580 (m)	1590 (m)	Aromatic C-C multiple band.
1410 (s)	1455 (m)	1420 (mw)	Aromatic C-C multiple band.
-	1480 (m)	1460 (s)	Sym. C=O Stretching.
-	1350 (m)	1300 (m)	C-O Stretching.
1320 (w)	1310 (m)	1260 (w)	C-N Stretching. (Py.)
-	1265 (m)	1230 (m)	C-N Stretching. (Py.)
1170 (s)	1170 (m)	1160 (w)	Py. ring.
-	1035 (s)	1050 (w)	C-O Stretching.
-	910 (s)	-	OH deformation.
-	-	860 (mb)	Coordinated H ₂ O mol.
810 (s)	850 (w)	830 (m)	Out of plane CH bending.
750 (w)	745 (m)	760(mb)	Out of plane CH bending.
740 (s)	-	735 (sh)	Out of plane CH bending.
-	690 (m)	-	COOH Wagging mode.
-	-	685 (mb)	Coordinated H ₂ O mol.
680 (wb)	650 (m)	680 (wm)	Out of plane CH bending.
610 (wb)	600 (m)	600 (w)	Py. ring deformation.
-	520 (s)	-	COOH Wagging mode.
-	-	450 (mb)	M-O Stretching.
-	-	380 (wm)	M-N Stretching.

TABLE - 4.08

IR SPECTRAL DATA OF dipy./ HBAA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	HBAA	Cu (dipy.) HBAA	Probable assignments
-	-	3400 (b)	Coordinated H ₂ O mol.
-	3450 (sb)	-	OH phenolic Stretching.
-	1640 (s)	1620 (s)	C=N Stretching. (Azomethine)
-	1700 (s)	1640 (s)	Asym. C=O Stretching.
1600 (s)	-	1560 (s)	C=N Stretching. (Py.)
1585 (m)	1580 (m)	1585 (sh)	Aromatic C=C multiple band.
1410 (s)	-	1410 (m)	Aromatic C=C multiple band.
-	1400 (m)	1390 (s)	Sym. C=O Stretching.
-	1370 (m)	1350 (m)	C-O Stretching.
1320 (w)	-	1310 (mw)	C-N Stretching. (Py.)
-	1365 (m)	-	OH phenolic bending.
-	1175 (m)	1170 (mw)	Phenolic CO Stretching.
1170 (s)	-	1165 (w)	Py. ring
-	1080 (w)	1070 (w)	Benzene breathing.
-	930 (w)	-	Oh deformation.
-	-	845 (wb)	Coordinated H ₂ O mol.
810 (s)	810 (m)	815 (s)	Out of plane CH bending.
750 (w)	755 (s)	750 (sb)	Out of plane CH bending.
740 (s)	-	740 (w)	Out of plane CH bending.
-	690 (w)	-	COOH bending.
-	675 (m)	690 (mb)	Coordinated H ₂ O mol.
680 (wb)	-	680 (wm)	Out of plane CH deformation.
610 (wb)	570 (m)	590 (w)	Py. ring deformation.
-	570 (wb)	-	COOH Wagging mode.
-	-	480 (wm)	M-O Stretching.
-	-	350 (m)	M-N Stretching.

TABLE - 4.09

IR SPECTRAL DATA OF dipy./ HBAT LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	HBAT	Cu (dipy.) HBAT	Probable assignments
-	-	3490 (mb)	Coordinated H ₂ O mol.
-	3250 (w)	-	OH phenolic Stretching
-	2550 (w)	-	S-H Stretching.
-	1635 (s)	1605 (m)	C=N Stretching. (Azomethine).
1600 (s)	-	1540 (w)	C=N Stretching. (Py.)
1585 (m)	1580 (m)	1590 (s)	Aromatic C-C multiple band.
1410 (s)	1440 (s)	1450 (mw)	Aromatic C-C multiple band.
-	1360 (m)	-	C-H phenolic bending.
1320 (w)	-	1310 (m)	Sym. C=O Stretching.
-	1175 (w)	1120 (m)	C-O Stretching.
1170 (s)	-	1160 (wm)	C-N Stretching. (Py.)
-	960 (w)	965 (w)	OH phenolic bending.
-	-	840 (mb)	Phenolic CO Stretching.
810 (s)	880 (m)	-	Py. ring
750 (w)	750 (s)	755 (s)	Benzene breathing.
740 (s)	-	735 (m)	Oh deformation.
680 (wb)	695 (w)	690 (s)	Coordinated H ₂ O mol.
-	-	685 (m)	Out of plane CH bending.
-	660 (w)	630 (m)	Out of plane CH bending.
610 (wb)	-	600 (wm)	Out of plane CH bending.
-	-	450 (wm)	COOH bending.
-	-	400(m)	Coordinated H ₂ O mol.
-	-	345 (w)	Out of plane CH deformation.
			Py. ring deformation.
			COOH Wagging mode.
			M-O Stretching.
			M-N Stretching.

TABLE – 4.10

IR SPECTRAL DATA OF dipy./ DNSA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DNSA	Cu (dipy.) DNSA	Probable assignments
-	3490 (m)	-	OH phenolic Stretching
-	1660 (s)	1620 (sb)	Asym. C=O Stretching
1585 (m)	1600 (m)	1580 (m)	Aromatic C-C multiple band
1600 (s)	-	1560 (s)	C=N Stretching. (Py)
-	1530 (s)	1530 (s)	Aromatic NO ₂ group.
-	1440 (m)	1380 (s)	Sym. C=O Stretching.
1410 (s)	-	1410 (m)	Aromatic C-C multiple band
-	1380 (m)	1360 (mw)	C-O Stretching.
-	1370 (m)	-	OH phenolic bending.
1320 (w)	1330 (m)	1310 (s)	C-N Stretching.
-	1255 (s)	1265 (m)	C-N Stretching.
-	1170 (w)	1160 (m)	Phenolic CO Stretching.
1170 (w)	-	1165 (s)	Py. ring
-	1100 (w)	1090 (w)	Benzene breathing.
-	1050 (w)	1060 (wb)	C-O Stretching.
-	950 (w)	960 (wm)	Benzene breathing.
-	930 (m)	-	OH deformation.
810 (s)	850 (mb)	820 (s)	Out of plane CH bending.
750 (w)	740 (s)	745 (m)	Out of plane CH bending.
740 (s)	-	-	Out of plane CH bending.
680 (wb)	720 9m)	710 (m)	Out of plane CH bending.
-	685 (m)	-	COOH bending.
610 (wb)	-	620 (m)	Py. Ring deformation.
-	515 (wb)	-	COOH wagging mode.
-	-	370 (m)	M-O Stretching.
-	-	320 (m)	M-N Stretching.

TABLE - 4.11

IR SPECTRAL DATA OF dipy./ DBSA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DBSA	Cu (dipy.) DBSA	Probable assignments
-	3240 (m)	-	OH phenolic Stretching
-	1670 (sb)	1620 (s)	Asym. C=O Stretching
1600 (s)	-	1560 (s)	C=N Stretching. (Py.)
1585 (m)	1590 (m)	1600 (m)	Aromatic C-C multiple band
1410 (s)	-	1410 (m)	Aromatic C-C multiple band
-	1420 (m)	1475 (sb)	Sym. C=O Stretching.
-	1380 (mb)	-	OH phenolic bending.
-	1350 (w)	1340(m)	C-O Stretching.
1320 (w)	-	1290 (m)	C-N Stretching.
-	1180 (w)	1130 (w)	Phenolic CO Stretching.
1170 (w)	-	1180 (w)	Py. ring
-	1100(w)	1095 (w)	Benzene breathing.
-	910 (w)	-	OH deformation.
810 (s)	800(mb)	870 (mb)	Out of plane CH bending.
-	-	810 (s)	-
750 (w)	780(w)	750 (s)	Out of plane CH bending.
740 (s)	-	740 (m)	Out of plane CH bending.
680 (wb)	710 (m)	700(wb)	Out of plane CH bending.
-	660 wb)	660(wb)	Out of plane CH bending.
-	685 (w)	-	COOH bending.
610 (wb)	-	640 (m)	Py. Ring deformation.
-	600 (m)	605 (m)	C-Br. Stretchig.
-	550(w)	-	COOH wagging mode.
-	470 (s)	475(m)	C-Br. Stretching.
-	-	440 (m)	M-O Stretching.
-	-	370(m)	M-N Stretching.

TABLE - 4.12

IR SPECTRAL DATA OF dipy./ HNA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	HNA	Cu (dipy.)HNA	Probable assignments
-	3450 (w)	-	OH phenolic Stretching.
-	1670 (sb)	1620 (s)	Asym. C=O Stretching
1600 (s)	-	1610 (s)	C=N Stretching. (Py.)
1585 (m)	1585 (m)	1590 (sb)	Aromatic C-C multiple band
-	1480 (mb)	1440 (sb)	Sym. C=O Stretching.
1410 (s)	-	1410 (s)	Aromatic C-C multiple band.
-	1380 (m)	1340 (m)	C-O Stretching.
-	1375 (mb)	-	OH phenolic bending.
1320 (w)	-	130 (mw)	C-N Stretching.
-	1170 (m)	1210 (w)	Phenolic CO Stretching.
1170 (w)	-	1160 (m)	Py. ring
-	1100 (w)	1095 (w)	Benzene breathing.
-	1040 (w)	1030 (w)	C-O Stretching.
-	910 (w)	-	OH deformation.
810 (s)	800 (m)	815 (s)	Out of plane CH bending.
750 (w)	760 (w)	770 (m)	Out of plane CH bending.
740 (s)	-	740 (w)	Out of plane CH bending.
-	685 (w)	-	COOH bending.
680 (wb)	660 (m)	650 (m)	Out of plane CH deformation.
610 (wb)	-	635 (w)	Py. Ring deformation.
-	550 (m)	-	COOH wagging mode.
-	-	440 (wm)	M-O Stretching.
-	-	380 (m)	M-N Stretching.

TABLE - 4.13

IR SPECTRAL DATA OF dipy./ IMDA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	IMDA	Cu (dipy.) IMDA	Probable assignments
-	-	3470 (mb)	Coordinated H ₂ O mol.
-	3400 (s)	3360 (m)	N-H Stretching.
-	1690 (sb)	1640 (sb)	Asym. C=O Stretching.
1600 (s)	-	1585 (sb)	C=N Stretching. (Py.)
1585 (m)	-	1580 (m)	Aromatic C-C multiple band.
-	1585 (mb)	1370 (m)	N-H Bending.
-	1400 (mb)	1380 (s)	Sym. C=O Stretching.
1410 (s)	-	1415 (m)	Aromatic C-C multiple band
-	1385 (mb)	-	C-O Stretching.
1320 (w)	1310 (w)	1300 (s)	C-N Stretching.
-	1250 (wb)	1210 (m)	C-N Stretching.
1170 (w)	-	1160 (w)	Py. ring
-	1060 (w)	1040 (m)	C-O Stretching.
-	-	-	OH deformation.
-	930 (m)	830 (m)	Coordinated H ₂ O mol.
810 (s)	-	-	Out of plane CH bending.
750 (w)	850 (m)	-	Out of plane CH bending.
740 (s)	-	735 (m)	Out of plane CH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
680 (wb)	680 (s)	685 (w)	Out of plane CH deformation.
610 (wb)	-	640 (m)	Py. Ring deformation.
-	565 (m)	-	COOH Wagging Mode.
-	550 (s)	-	COOH Wagging Mode.
-	-	410 (m)	M-O Stretching.
-	-	320 (m)	M-N Stretching.

TABLE - 4.14

IR SPECTRAL DATA OF dipy./ DPDC LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DPDC	Cu (dipy.) DPDC	Probable assignments
-	-	3480 (mb)	Coordinated H ₂ O mol.
-	3400 (w)	3370 (w)	N-H Stretching.
-	1660 (s)	1610 (s)	Asym. C=O Stretching.
1600 (s)	-	1575 (s)	C=N Stretching. (Py.)
1585 (m)	1580 (m)	-	Aromatic C-C multiple band.
-	1585 (m)	1560 (s)	N-H Bending.
1410 (s)	1450 (m)	1555 (s)	Aromatic C-C multiple band.
-	1440 (m)	1420 (sb)	Sym. C=O Stretching.
-	1345 (s)	1320 (w)	C-O Stretching.
1320 (w)	1310 (m)	1285 (w)	C-N Stretching.
-	1275 (w)	1230 (m)	C-N Stretching.
1170 (w)	-	1165 (m)	Py. ring
-	1075 (m)	1075 (w)	Benzen breathing.
-	920 (s)	-	OH deformation.
-	-	860 (mb)	Coordinated H ₂ O mol.
810 (s)	810 (m)	815 (s)	Out of plane CH bending.
750 (w)	785 (m)	765 (s)	Out of plane CH bending.
740 (s)	740 (s)	730 (w)	Out of plane CH bending.
680 (wb)	710 (m)	715 (wb)	Out of plane CH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
-	650 (m)	660 (w)	Coordinated H ₂ O mol.
-	680 (m)	-	COOH bending.
610 (wb)	-	630 (mb)	Py. Ring deformation.
-	550 (m)	-	COOH wagging mode.
-	-	470 (m)	M-O Stretching.
-	-	400 (m)	M-N Stretching.

In free TDPA, TDAP and DTPA frequencies in the region of 2930 cm^{-1} to 2850 cm^{-1} are observed due to asymmetric and symmetric $\text{CH}_2\text{-S}$ stretching vibration. In the complexes with Cu (II) (dipy), both frequencies shift to a lower region. Hence, the metal must have linked to ligand through S of CH_2S group.

The free MBA and HBAT exhibit weak spectral bands at 2550 cm^{-1} and 2590 cm^{-1} respectively due to stretching of -SH group. However, the frequencies disappear in complexation with Cu (dipy). -SH group is deprotonated to form a Cu (II) to MBA on HBAT bond respectively.

The $\nu_{\text{C}=\text{N}}$ of azomethine group in HBA and HBAAT manifests as sharp spectral bands at 1640 cm^{-1} and 1635 cm^{-1} respectively. However, on ternary complex formation, as described, the frequencies are lowered by $20\text{-}50\text{ cm}^{-1}$. The lowering of frequency is attributed to the coordination of the ligand to Cu(II) through nitrogen of a azomethine group as noted by earlier investigators.

The $\nu_{\text{C}=\text{N}}$ vibration of pyridyl group in dipy and PDA occurs as moderate spectral band in the region of 1600 cm^{-1} . In the case of Cu (dipy) PDA and Cu (dipy) HNA, these are shifted to higher frequencies by about 15 cm^{-1} . In other complexes, there is a shift $10\text{-}75\text{ cm}^{-1}$ in the lower direction. This relocation $\nu_{\text{C}=\text{N}}$ frequency is indication of participation of N of pyridine in complex.

The C-H bending and deformation bands at $850\text{-}620\text{ cm}^{-1}$ and ring system band at $1150\text{-}1000\text{ cm}^{-1}$ have been observed in all the cases.

Weak moderate bands at 590 cm^{-1} (for free TDPA and DTSA), at 570 cm^{-1} (for free MBA and TDAA) and at 660 cm^{-1} (for DTPA and HBAT) are attributed to

C-S vibrations. These vibrations are shifted to a lower frequency region by a margin of $10\text{-}40\text{ cm}^{-1}$ in the Cu (II) (dipy). complexes. It establishes that coordination has taken place through S of the C-S group.

Vibrations due S-S stretching are observed as spectral bands at $500\text{ - }510\text{ cm}^{-1}$ for free DTSA and DTPA respectively. These frequencies too undergo a negative shift by $10\text{-}30\text{ cm}^{-1}$. This is further confirmation that coordination has occurred via that 'S' atom. Finally the appearance of bands corresponding $\nu_{\text{Cu-O}}$, $\nu_{\text{Cu-N}}$ and $\nu_{\text{Cu-S}}$ in regions around 440cm^{-1} , 350cm^{-1} and 400 cm^{-1} respectively makes it obvious that ternary complexes do contain Cu-O, Cu-N and Cu-S linkages.

A broad band in the region $3280\text{-}3500\text{ cm}^{-1}$ in Cu (dipy.) ternary complexes with TDPA, TDAA, PDA, HBAA, HBAT and DPDC is attributed to the stretching frequency of O-H of the coordinated water. In these complexes, moderate bands in the region $820\text{-}860\text{ cm}^{-1}$ and $680\text{-}690\text{cm}^{-1}$ are also discernible. It may be attributed to rocking and bending vibrations of O-H as observed by Nakamoto¹¹. Further, negligible loss in weight of these complexes, when heated, in the range of $120\text{ - }180^{\circ}\text{C}$ reinforces the finding that water molecules are coordinated to the central metal copper (II).

On the other hand, the ternary complexes of Cu(dipy) with DTPA, although contains water indicated by a broad absorption band at 3450 cm^{-1} does not have it in coordinated form¹¹ as it was not possible to locate a band due to binding and rocking vibration in the region $840 \pm 10\text{cm}^{-1}$.

4.2.2 Ternary complexes with Cu (phen)

The important infrared frequencies of the ligands and Cu (II)- (phen.) 1:1:1 ternary complexes have been summarized in table 4.15 to 4.22. The tables also include tentative comments about the assignment of some bands. It would be in place to discuss some prominent peaks vital from the point of view of establishment of structure and bonding in the ternary complexes under investigation. Obviously a 4,7-dimethyl-1,10-phenanthroline (phen.) is a common ligand in all these complexes of copper (II). As in the case of Cu (II) (dipy) complexes with the other ligands, significant shifting of the peaks of ligands is discernible when they form complexes under study.

Two sets of moderate bands at 3450cm^{-1} , 3250cm^{-1} , 3490cm^{-1} , 3240cm^{-1} and 1365cm^{-1} , 1360cm^{-1} , 1370cm^{-1} and 1380cm^{-1} are attributed to stretching and bending frequencies of phenolic -OH group present in HBAA, HBAT, DNSA and DBSA respectively. But in the corresponding 1:1:1 complexes, these bands disappear leading us to the conclusion the Cu(II) - ligand bond has occurred by displacement of proton from OH group to form Cu (II)-O-C bond.

The asymmetric and symmetric stretching vibration in $\text{CH}_2\text{-S}$ group manifests it self as infrared spectral bands at 2930cm^{-1} and 2850cm^{-1} for DTPA. In the corresponding Cu (II) (Phen) (DTPA) ternary complex, a lowering in frequency in the range of 40cm^{-1} is observed for both the bands. It may be therefore, concluded that S atom of $\text{CH}_2\text{-S}$ group of DTPA coordinates directly with copper (II).

TABLE - 4.15

IR SPECTRAL DATA OF dipy./ MBA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	MBA	Cu (dipy.) MBA	Probable assignments
-	-	-	Coordinated H ₂ O mol.
-	2590 (m)	-	S-H Stretching.
-	1690 (s)	1580 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1560 (s)	Aromatic C-C multiple band.
1600 (s)	-	1525 (m)	C=N Stretching. (Py.)
1500 (m)	1450 (m)	1430 (m)	Aromatic C-C multiple band.
-	1420 (m)	1380 (s)	Sym. C=O Stretching.
1340 (s)	-	1355 (w)	C-N Stretching. (Py.)
1250 (s)	-	1160 (m)	C-N Stretching. (Py.)
1165 (w)	-	1140 (m)	Py. ring
1060 (w)	1060 (w)	-	Benzene breathing.
-	1050 (w)	1035 (m)	C-O Stretching.
-	930 (m)	-	O-H Stretching.
-	-	-	Coordinated H ₂ O mol.
800 (s)	910 (m)	820 (s)	Out of plane CH bending.
700 (w)	740 (ms)	740 (m)	Out of plane CH bending.
-	-	-	Coordinated H ₂ O mol.
665 (w)	660 (m)	680 (w)	Out of plane CH bending.
-	680 (m)	-	COOH bending.
630 (w)	-	620 (w)	Py. Ring deformation.
-	570 (m)	565 (m)	C-S Stretching.
-	520 (w)	-	COOH wagging mode.
-	-	410 (w)	M-O Stretching.
-	-	330 (m)	M-N Stretching.
-	-	280 (w)	M-S Stretching.

TABLE - 4.16

IR SPECTRAL DATA OF phen./ DTSA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DTSA	Cu (dipy.) DTSA	Probable assignments
-	1680 (s)	1600 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1580 (m)	Aromatic C-C multiple band.
1600 (s)	-	1540 (m)	C=N Stretching. (Py.)
1500 (m)	1480 (m)	1480 (m)	Aromatic C-C multiple band.
-	1415 (s)	1385 (w)	Asym. C=O Stretching.
-	1360 (m)	-	C-O Stretching.
1340 (s)	-	-	C-N Stretching. (Py.)
1250 (s)	-	1220 (s)	C-N Stretching. (Py.)
1165 (w)	-	1140 (m)	Py. ring
1060 (w)	1100 (w)	1100 (s)	Benzene breathing.
800 (s)	920 (s)	-	OH deformation.
700 (w)	790 (m)	790 (w)	Out of plane CH bending.
-	730 (s)	740 (w)	Out of plane CH bending.
665 (w)	680 (m)	-	COOH bending.
-	650 (m)	660 (mb)	Out of plane CH deformation.
630 (w)	650 (m)	625 (w)	C-S Stretching.
-	-	620 (s)	Py. Ring deformation.
-	555 (s)	-	COOH wagging. mode.
-	500 (w)	460 (w)	S-S Stretching.
-	-	420 (wb)	M-O Stretching.
-	-	325 (w)	M-N Stretching.
-	-	290 (m)	M-S Stretching.

TABLE - 4.17

IR SPECTRAL DATA OF phen./ DTPA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DTPA	Cu (dipy.)DTPA	Probable assignments
-	2930 (s)	2890 (m)	Asym. CH ₂ -S Stretching.
-	2850 (s)	2810 (w)	Sym. CH ₂ -S Stretching.
-	1700 (s)	1640 (s)	Asym. C=O Stretching.
1670 (m)	-	1675 (w)	Aromatic C-C multiple band.
1600 (s)	-	1520 (m)	C=N Stretching. (Py.)
1500 (m)	-	1500(w)	Aromatic C-C multiple band.
-	1420 (s)	1410 (s)	Sym. C=O Stretching.
-	1410 (s)	1440 (s)	CH ₂ -S deformation.
-	1365 (m)	1330 (m)	C-O Stretching.
1340 (s)	-	1290 (m)	C-N Stretching (Py.)
-	1260 (s)	1220 (m)	CH ₂ -S Wagging.
1250 (s)	-	-	C-N Stretching. (Py.)
1165 (w)	-	1160 (m)	Py. ring
1060 (w)	-	1060 (w)	Benzene breathing.
-	1035 (w)	1000 (w)	C-O Stretching.
-	930 (s)	-	OH deformation.
800 (s)	790 (m)	840 (m)	Out of plane CH bending.
700 (w)	-	770 (w)	Out of plane CH bending.
665 (w)	650 (m)	660 (w)	Out of plane CH deformation.
-	660 (w)	640 (m)	C-S Stretching.
630 (w)	-	620 (wb)	Py. Ring deformation.
-	550 (m)	-	COOH wagging. mode.
-	510 (m)	480 (mb)	S-S Stretching.
-	-	390 (m)	M-O Stretching.
-	-	340 (m)	M-N Stretching.
-	-	300(w)	M-S Stretching.

TABLE - 4.18

IR SPECTRAL DATA OF phen./ PDA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	PDA	Cu (dipy.) PDA	Probable assignments
-	-	3460 (sb)	Coordinated H ₂ O mol.
-	1700 (s)	1670 (s)	Asym. C=O Stretching.
1670 (m)	1580 (m)	1600 (m)	Aromatic C-C multiple band.
1600 (s)	1600 (s)	1580 (m)	C=N Stretching. (Py.)
1500 (m)	1460 (m)	1440 (m)	Aromatic C-C multiple band.
-	1420 (m)	1370 (s)	Sym. C=O Stretching.
-	1350 (s)	1300 (w)	C-O Stretching.
1340 (s)	1310 (s)	1290 (w)	C-N Stretching (Py.)
1250 (s)	1265 (s)	1200 (m)	C-N Stretching (Py.)
1165 (w)	1165 (m)	1150 (m)	Py. ring
1060 (w)	-	1070 (m)	Benzene breathing.
-	1035 (m)	1030 (w)	C-O Stretching.
-	930 (m)	-	OH Stretching.
-	-	-	Coordinated H ₂ O mol.
800 (s)	800 (s)	790 (m)	Out of plane CH bending.
700 (w)	740 (w)	750 (w)	Out of plane CH bending.
-	690 (m)	-	CHOO bending.
-	-	685 (m)	Coordinated H ₂ O mol.
665 (w)	650 (m)	670 (w)	Out of plane CH deformation.
630 (w)	600 (m)	625 (wb)	Py. Ring deformation.
-	520 (s)	-	COOH wagging mode.
-	-	450 (m)	M-O Stretching.
-	-	330 (w)	M-N Stretching.

TABLE - 4.19

IR SPECTRAL DATA OF phen./ HBAA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	HBAA	Cu (dipy.) HBAA	Probable assignments
-	-	3460 (mb)	Coordinated H ₂ O mol.
-	3450 (w)	-	OH phenolic Stretching.
1670 (m)	-	-	Aromatic C-C multiple band.
-	1640 (s)	1600 (s)	C=N Stretching. (Py.)
-	1620 (s)	1560 (s)	Asym. C=O Stretching.
1600 (s)	-	1540 (s)	C=N Stretching.
1500 (m)	1580 (m)	1505(m)	Aromatic C-C multiple band.
-	1400 (m)	1360 (s)	Sym. C=O Stretching.
-	1370 (w)	1345 (sb)	C-O Stretching.
-	1365 (m)	-	OH phenolic bending.
1340 (s)	-	1310 (sb)	C-N Stretching (Py.)
1250 (s)	-	1230 (w)	C-N Stretching (Py.)
-	-	1140 (m)	Phenolic CO Stretching.
1165 (w)	1175 (w)	1170 (w)	Py. ring
1060 (w)	-	1050 (w)	Benzene breathing.
-	1070 (w)	-	OH deformation.
-	925 (w)	845 (m)	Coordinated H ₂ O mol.
800 (s)	-	810 (wb)	Out of plane CH bending.
700 (w)	810 (m)	750 (mb)	Out of plane CH bending.
-	755 (s)	690 (w)	Coordinated H ₂ O mol.
-	-	-	CHOO bending.
665 (w)	690 (w)	665 (w)	Out of plane CH deformation.
630 (w)	675 (m)	620 (m)	Py. Ring deformation.
-	-	-	COOH wagging mode.
-	570 (wb)	440 (w)	M-O Stretching.
-	-	325 (m)	M-N Stretching.

TABLE - 4.20

IR SPECTRAL DATA OF phen./ HBAT LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	HBAT	Cu (dipy.) HBAT	Probable assignments
-	-	3450 (mb)	Coordinated H ₂ O mol.
-	3250 (m)	-	OH phenolic Stretching.
-	2550 (w)	-	S-H Stretching.
1670 (m)	-	1600 (s)	Aromatic C-C multiple band.
-	1640 (s)	1610 (s)	C=N Stretching. (Azomethine.)
1600 (s)	-	1540 (s)	C=N Stretching. (Py.)
1500 (m)	1580 (m)	1560 (s)	Aromatic C-C multiple band.
-	1440 (s)	1445 (w)	Aromatic C.C multiple band.
-	1360 (m)	-	OH phenolic bending.
1340 (s)	-	1310 (w)	C-N Stretching (Py.)
1250 (s)	-	1230 (m)	C-N Stretching (Py.)
-	1170 (w)	1140 (w)	Phenolic CO Stretching.
1165 (w)	-	1160 (m)	Py. ring
1060 (w)	960 (m)	-	Benzene breathing.
800 (s)	850 (w)	840 (m)	Out of plane CH bending.
-	-	810 (mb)	Coordinated H ₂ O mol.
700 (w)	740 (s)	730 (s)	Out of plane CH bending.
-	-	685 (wb)	Coordinated H ₂ O mol.
665 (w)	690 (m)	675 (w)	Out of plane CH deformation.
-	660 (w)	635 (m)	C-S Stretching.
630 (w)	-	620 (w)	Py. Ring deformation.
-	-	460 (w)	M-O Stretching.
-	-	390 (m)	M-N Stretching.
-	-	340 (m)	M-S Stretching.

TABLE - 4.21

IR SPECTRAL DATA OF phen./ DNSA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DNSA	Cu (dipy.) DNSA	Probable assignments
-	-	-	Coordinated H ₂ O mol.
-	3490 (m)	-	OH phenolic Stretching.
-	1680 (s)	1610 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1600 (s)	Aromatic C-C multiple band.
1600 (s)	-	1560(s)	C=N Stretching.
1500 (m)	-	1490 (s)	Aromatic C-C multiple band.
-	1470 (s)	1450 (s)	Sym. C=O Stretching.
-	1380 (m)	1350 (sb)	C-O Stretching.
-	1370 (m)	-	OH phenolic Stretching.
1340 (s)	1330 (m)	1320 (s)	C-N Stretching (Py.)
1250 (s)	1255 (b)	1185 (m)	C-N Stretching (Py.)
-	1175 (w)	1100 (m)	Phenolic CO Stretching.
1165 (w)	-	1155 (w)	Py. ring
1060 (w)	1090 (w)	-	Benzene breathing.
-	1050 (w)	1000 (w)	C-O Stretching.
-	960 (w)	970 (w)	Benzene breathing.
-	930 (w)	-	OH deformation.
-	-	-	Coordinated H ₂ O mol.
800 (s)	840 (m)	820 (m)	Out of plane CH bending.
700 (w)	730 (m)	-	Out of plane CH bending.
665 (w)	715 (mb)	710 (m)	Out of plane CH deformation.
630 (w)	680 (s)	680 (m)	Py. Ring deformation.
-	-	-	Coordinated H ₂ O mol.
-	515 (mb)	-	COOH wagging mode.
-	-	400 (m)	M-O Stretching.
-	-	380 (m)	M-N Stretching.

TABLE - 4.22

IR SPECTRAL DATA OF phen./ DBSA LIGANDS AND THEIR Copper COMPLEX

Wave number (cm ⁻¹)			
Dipy.	DBSA	Cu (dipy.) DBSA	Probable assignments
-	-	-	Coordinated H ₂ O mol.
-	3240 (w)	-	OH phenolic Stretching.
-	1670 (sb)	1585 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1600 (m)	Aromatic C-C multiple band.
1600 (s)	-	1540 (s)	C-N Stretching. (Py.)
1500 (m)	-	-	Aromatic C-C multiple band.
-	1420 (mb)	1450 (sb)	Sym. C=O Stretching.
-	1380 (m)	-	OH phenolic Stretching.
-	1350 (w)	1310 (sb)	C-O Stretching.
1340 (s)	-	1270 (s)	C-N Stretching (Py.)
1250 (s)	-	1220 (w)	C-N Stretching (Py.)
-	1170 (w)	1130 (w)	Phenolic CO Stretching.
1165 (w)	-	1155 (w)	Py. ring
1060 (w)	1100 (w)	1100 (w)	Benzene breathing.
-	915 (w)	-	OH deformation.
-	-	-	Coordinated H ₂ O mol.
800 (s)	860 (mb)	870 (w)	Out of plane CH bending.
770 (w)	770 (w)	790 (m)	Out of plane CH bending.
665 (w)	720 (w)	720 (s)	Out of plane CH deformation.
-	-	-	Coordinated H ₂ O mol.
-	600 (m)	640 (w)	Coordinated H ₂ O mol.
-	690 (m)	-	COOH wagging mode.
630 (w)	-	-	Py. Ring deformation.
-	600 (m)	-	C-Br Stretching.
-	550 (w)	-	COOH Wagging mode.
-	470 (s)	475 (wb)	C-Br Stretching.
-	-	400 (m)	M-O Stretching.
-	-	330 (m)	M-N Stretching.

However, weak spectral bands at 2590 cm^{-1} and 2500 cm^{-1} due to S-H stretching vibration exhibited in IR spectra of MBA and HBAT. On ternary complex formation, with copper (II) these bands are found to disappear. As in phenolic – OH, here too, it may be concluded that proton of – SH group is replaced by the Cu (II) ion.

Free carboxylic ligands show sharp bands in the region of $1620 - 1700\text{ cm}^{-1}$ and $1400 - 1475\text{ cm}^{-1}$ in CO for asymmetric and symmetric stretching vibration respectively. The deformation of –OH group of the carboxylic part is depicted by a band in the region of 920 cm^{-1} . On ternary complex formation with Cu (II) (phen), there is a significant shift of CO stretching frequencies to the lower values. The –OH deformation vibrations disappear completely. It is a clear indication that bond formation has taken place through carboxylic group by deprotonation of the carboxylic – OH group

The stretching frequencies of $\text{C}\equiv\text{N}$ in azomethine group in free HBAA and HBAT are observed as sharp spectral bands at around 1640 cm^{-1} and 1635 cm^{-1} respectively. There is clear lowering of this frequency by at least 25 cm^{-1} in the corresponding complexes with Cu (II) (phen). Clearly, the N of the azomethine group is coordinating directly to the metal ion⁷⁻¹⁰.

In the free (phen) and PDA ligands, a sharp moderate band around 160 cm^{-1} is attributed to $\text{C}=\text{N}$ stretching vibration of pyridine group present. There is a notable shift in the frequency to a lower region on the formation of complexes. The nitrogen atom of pyridine in both the ligands, therefore, should be directly coordinating with the metal. As a matter of fact, the $\nu_{\text{C}=\text{N}}$ in pyridine and

frequency of pyridine ring deformation vibration also shifts to a lower region¹⁵⁻¹⁶. It is a clear confirmation of our conclusion that N atom of pyridine rings actually participates in ligand to metal coordinate bond.

The frequency of vibration due to the presence of pyridine ring is expected to be observed as a band at 1165 cm^{-1} . But it overlaps due to aromatic ring -C-C- and C=C vibration frequencies lying in the same region. Even this frequency is lowered by $10 - 25\text{ cm}^{-1}$ in all the ternary complexes of Cu (II) under study. It is now final that this ligand coordinates with the Cu (II) through its N atom.

Spectral bands at 570 cm^{-1} 650 cm^{-1} 660 cm^{-1} 660 cm^{-1} for C-S stretching frequency are observed MBA, DTSA, DTPA and HBAT ligands. There is a lowering of these frequencies in corresponding Cu(II) complexes. This is a clear evidence to conclude that S atom has participated in bond formation with the metal ion in all the four ternary Cu (phen.) complexes.

The S-S stretching frequencies in free DTSA and DTPA are observed as bands at 500 cm^{-1} and 510 cm^{-1} . This shifting to the extent of about 40 cm^{-1} in both the 1:1:1 complexes of Cu (II) is indicative¹⁷ of Cu – Sulphur bond being formed.

Some new bands are observed in the region of $395 - 480\text{ cm}^{-1}$ and $320 - 450\text{ cm}^{-1}$. These can be traced back to the formation of Cu-O and Cu-N bonds. Thus, it is safe to conclude that all the ligands coordinate through O and nitrogen atoms.

Appearance of IR bands at $850 - 620\text{ cm}^{-1}$ corresponding to out of plane C-H bending and deformation and $1150 - 1000\text{ cm}^{-1}$ corresponding to ring system are a common feature for all the ternary complexes that have been synthesized in the present investigations. The remaining peaks are due to the presence of aromatic rings and not relevant to our study.

In the ternary complexes of Cu (phen) with MBA, DBSA, PDA, HBAA, HBAT and DNSA, a broad band in the region of $3410 - 3580\text{ cm}^{-1}$ is attributed the O-H of the water molecules which are coordinated to Cu (II) ion. The presence of rocking and bending vibration of OH in the region of $8110 - 850\text{ cm}^{-1}$ and $680 - 690\text{ cm}^{-1}$ respectively reinforce our conclusion that H_2O molecules are coordinated to the metal ion. Further, on heating to $120 - 180^\circ\text{C}$ the weight of the ternary complexes remains constant. That means water molecules are present only as coordinated ligands and there is no lattices water in any one of these solid complexes.

4.3 Magnetic studies

As already discussed in an earlier chapter, the knowledge of effective magnetic moment of complex molecules lets us know the number of unpaired electrons and in most cases it helps to decide between different geometries of the complex. The knowledge of number of unpaired electrons may also help confirm geometry deduced from electronic spectral studies. The effective magnetic moment of all the Cu (II) ternary complexes has been summarized in table 4.23.

TABLE - 4.23

MAGNETIC MEASUREMENT DATA OF Cu (II) COMPLEXES

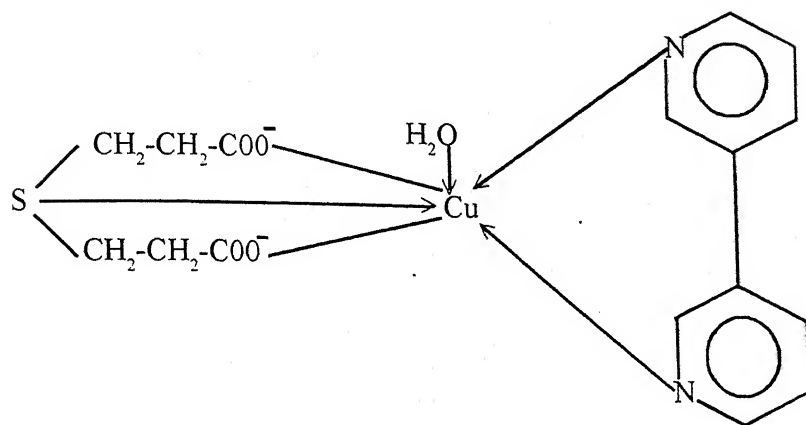
Compound	Molar susceptibility 'K _M ' = K' x M X 10 ⁻⁶	Diamagnetic correction (Dia) X 10 ⁻⁶	Corrected Molar susceptibility K _M (Dia) X 10 ⁻⁶	Curie's value 'C' = K _M (Dia) X 10 ⁻⁶ (T=300±2°K)	Magnetic susceptibility 'μ _{eff} ' = 2.84 √C(BM)	Number of unpaired e ⁻	Hybridization
Cu (dipy) TDPA. H ₂ O	1764.0293	-205	1969.0293	590708.79	2.18	1	sp ³ d ²
Cu (dipy) MBA	1140.4424	-183	1323.4424	394385.83	1.78	1	dsp ²
Cu (dipy) TDAA. H ₂ O	1298.1694	-181	1479.1694	446709.15	1.89	1	sp ³ d ²
Cu (dipy) DTSA	1734.0629	-260	1994.0629	598218.87	2.19	1	sp ³ d ²
Cu (dipy) DTPA	1639.8195	-209	1848.8195	554645.85	2.11	1	sp ³ d ²
Cu (dipy) DPA. H ₂ O	1436.5765	-185	1621.5765	489716.10	1.98	1	sp ³ d ²
Cu (dipy) HBAA. H ₂ O	903.10999	-246	1149.1099	347031.18	1.67	1	sp ³ d ²
Cu (dipy) HBAT. H ₂ O	1758.6493	-246	2004.6493	597385.49	2.19	1	dsp ²
Cu (dipy) DNSA	1160.0680	-182	1342.0680	399936.26	1.79	1	dsp ²
Cu (dipy) DBSA	1028.3221	-228	1256.3221	376896.63	1.74	1	dsp ²
Cu (dipy) HNA	1184.8256	-204	1388.8256	416647.68	1.83	1	sp ³ d ²
Cu (dipy) IMDA. H ₂ O	1140.3716	-185	1585.3716	475611.48	1.95	1	sp ³ d ²
Cu (dipy) DPDC. H ₂ O	1457.6333	-248	1705.6333	511689.99	2.03	1	sp ³ d ²
Cu (phen) MBA	1132.2620	-220	1352.2620	402974.07	1.80	1	dsp ²
Cu (phen) DTSA	1605.2391	-297	1902.2391	570671.73	2.14	1	dsp ²
Cu (phen) PDA. H ₂ O	1347.0894	-224	1571.0894	474468.99	1.95	1	dsp ²
Cu (phen) HBAA. H ₂ O	1595.2989	-284	1881.2989	564389.67	2.13	1	sp ³ d ²
Cu (phen) HBAT. H ₂ O	1700.5155	-286	1986.5155	599927.68	2.19	1	dsp ²
Cu (phen) DNSA	1082.1700	-232	1314.1700	396879.34	1.79	1	dsp ²
Cu (phen) DBSA	1030.1279	-265	1295.1279	391128.62	1.77	1	dsp ²
Cu (phen) DTPA	1230.4768	-246	1476.4768	445895.99	1.89	1	sp ³ d ²

A careful study of the table leads us to the conclusion that the effective magnetic moment values of all the complexes fall in the range of 1.67 to 2.19 BM. That means there is only one unpaired electron present in all the complexes. It implies that whether the geometry of the complex is square planar, tetrahedral or octahedral, the complex is expected to have only one unpaired electron. The range of magnetic moment is also indicator of monomeric nature of the Cu (II) complexes under study.

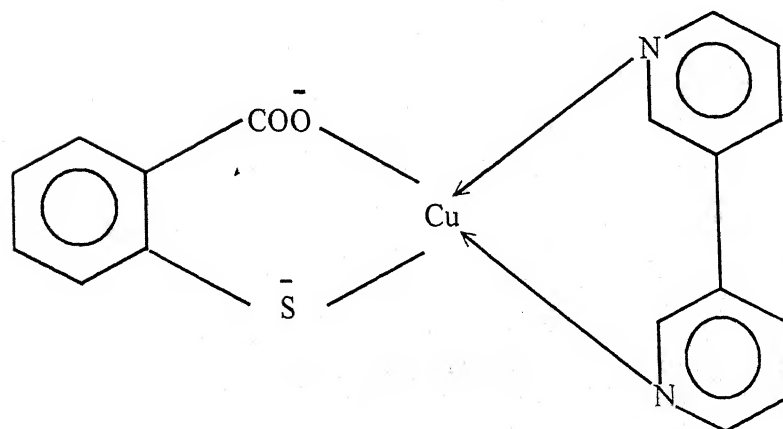
As far as differentiation between different shapes is concerned, the data obtained from magnetic studies is not of much help. However, it does not contradict the results of our electronic spectral investigations.

On the basis of the aforementioned discussion on spectral and magnetic studies, the structure of the ternary complexes may be depicted as shown in figures 4.1 to 4.6.

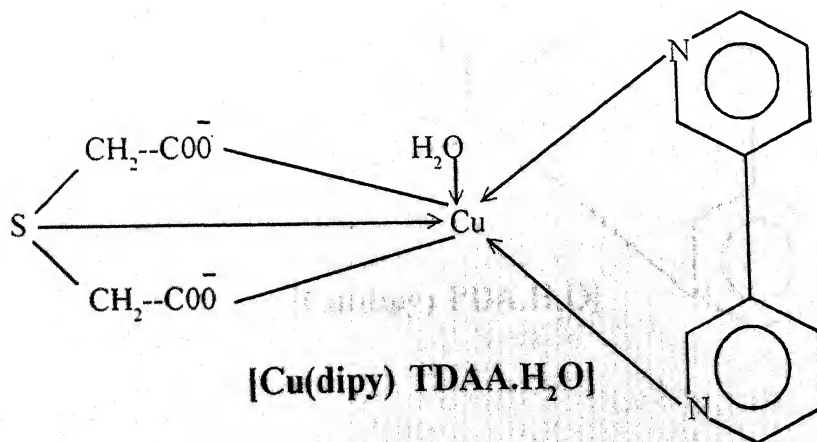
PROPOSED BONDING STRUCTURES OF DIPYRIDINE COPPER (II) COMPLEXES



[Cu(dipy) TDPA.H₂O]



[Cu(dipy) MBA]



[Cu(dipy) TDAA.H₂O]

FIGURE 4.1

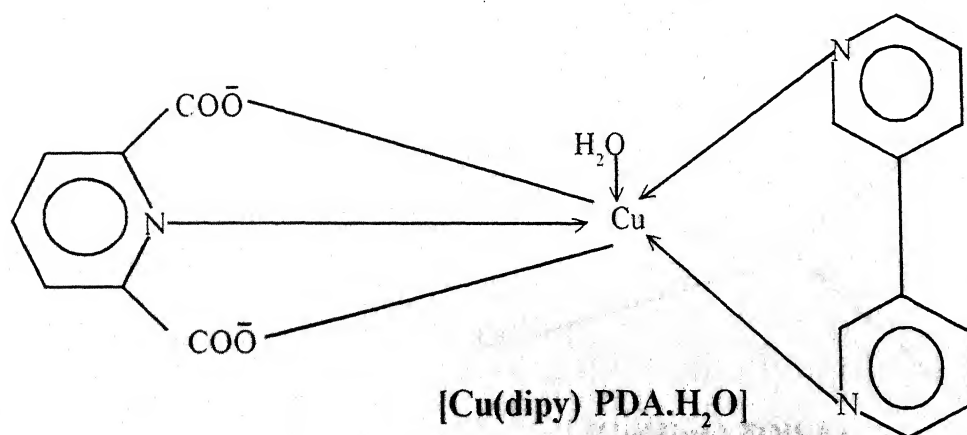
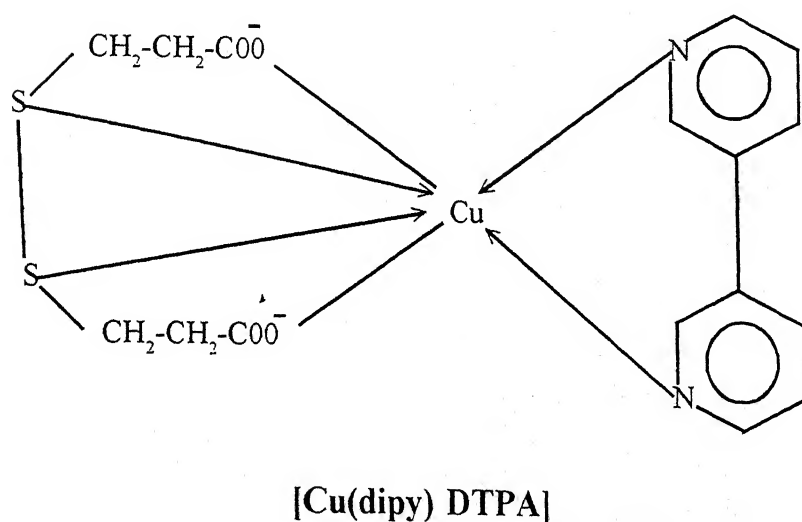
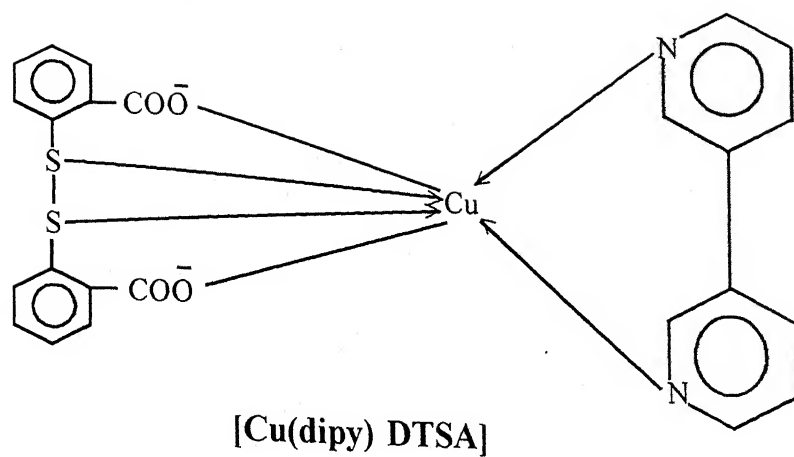
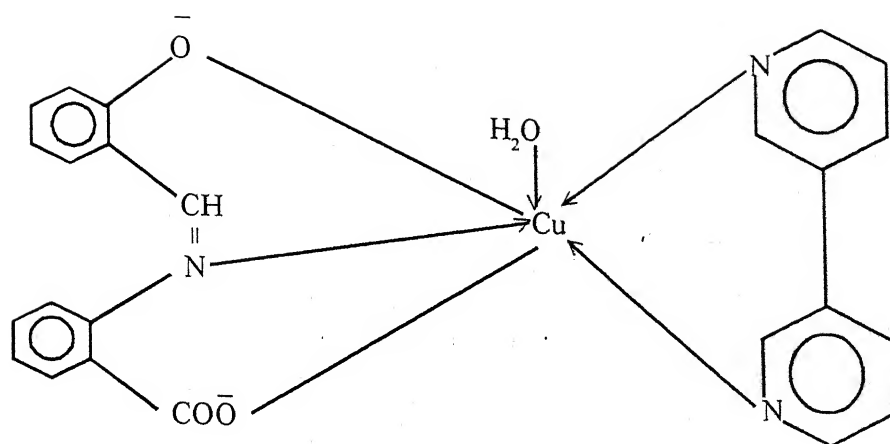
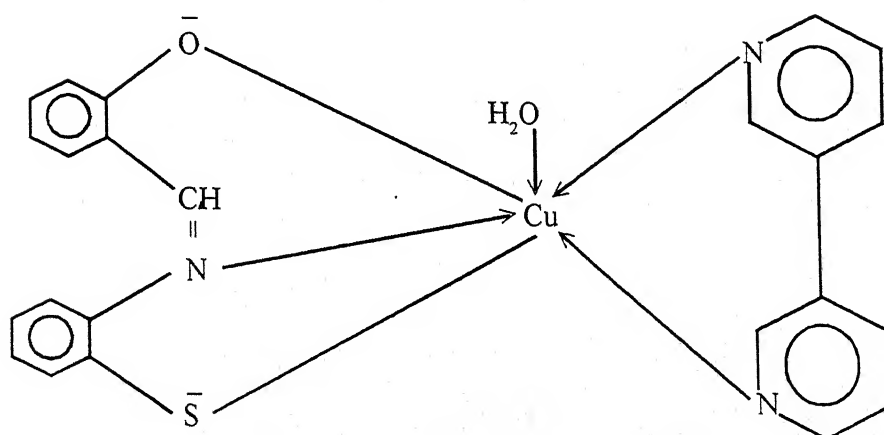


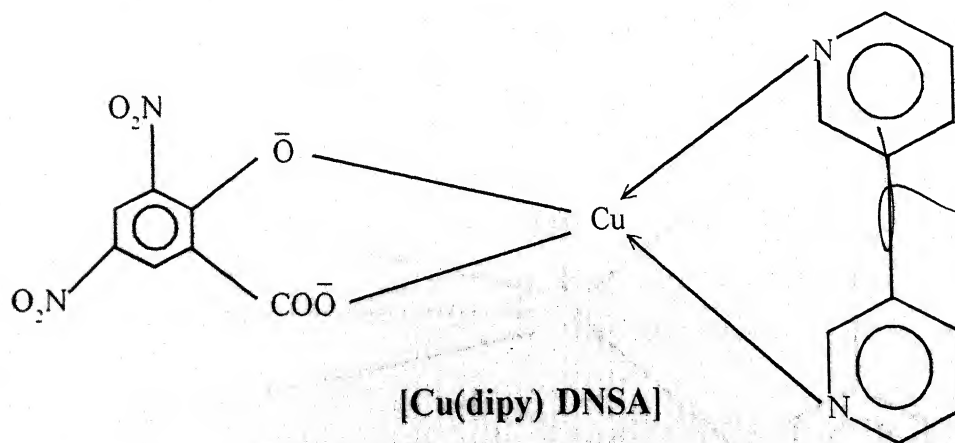
FIGURE 4.2



[Cu(dipy) HBAA.H₂O]



[Cu(dipy) HBA.T.H₂O]



[Cu(dipy) DNSA]

FIGURE 4.3

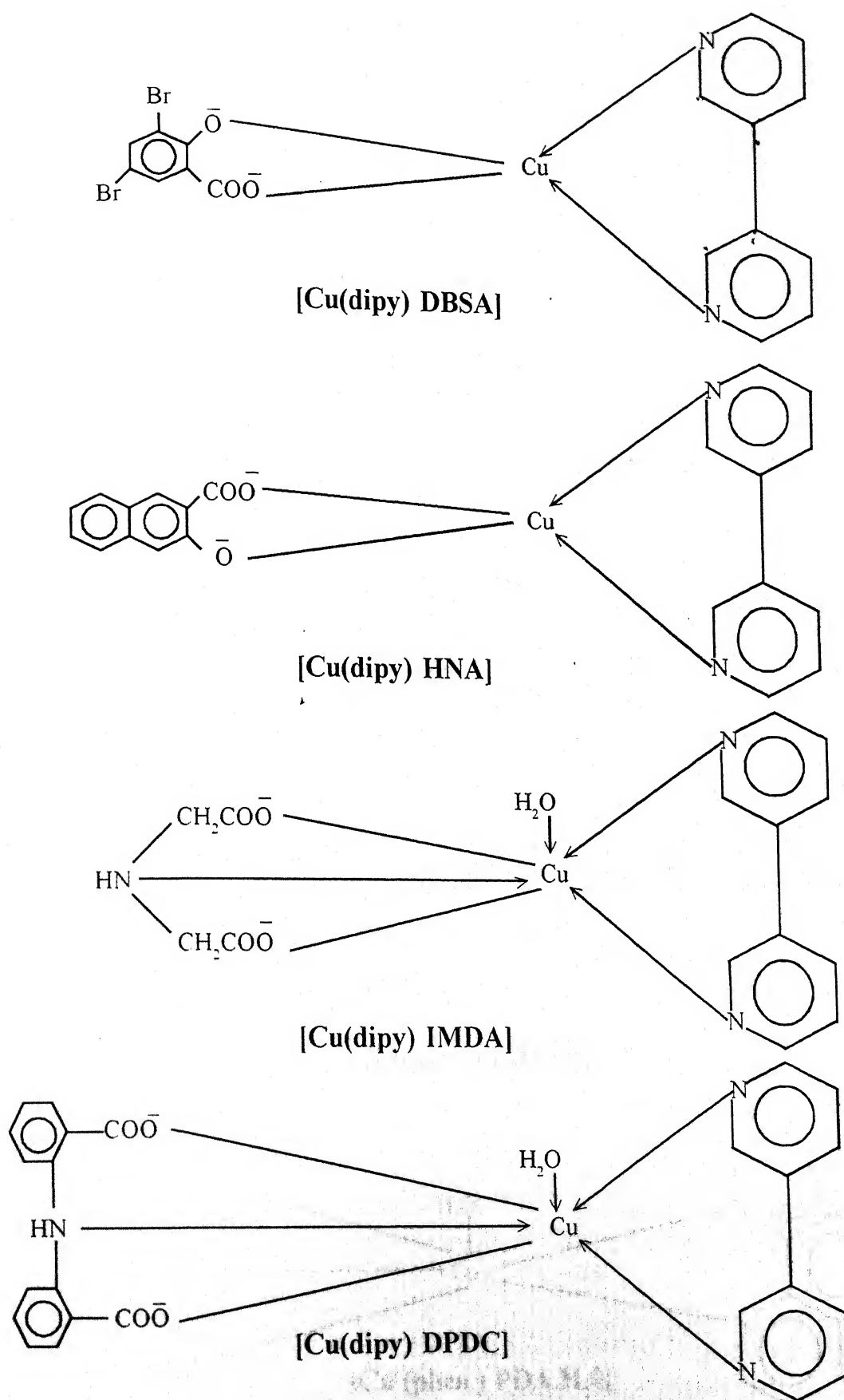


FIGURE 4.4

PROPOSED BONDING STRUCTURES OF PHENANTHROLINE COPPER (II) COMPLEXES

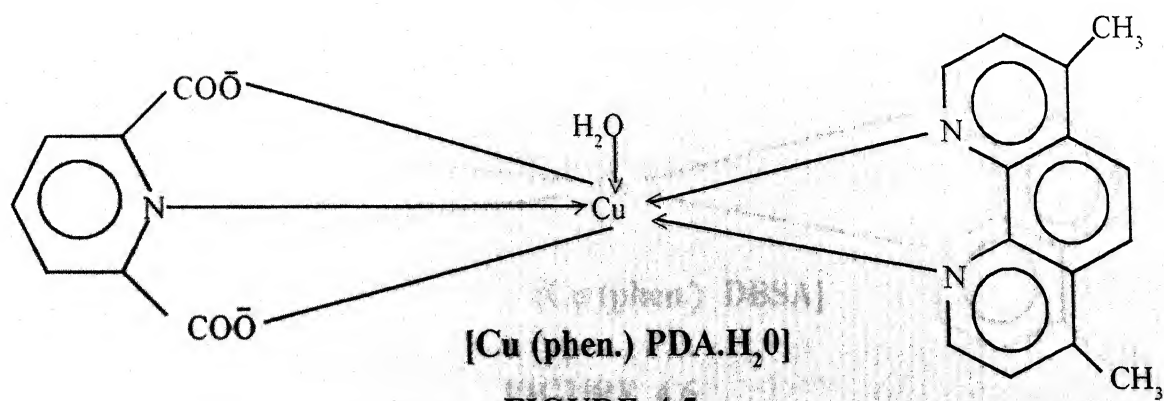
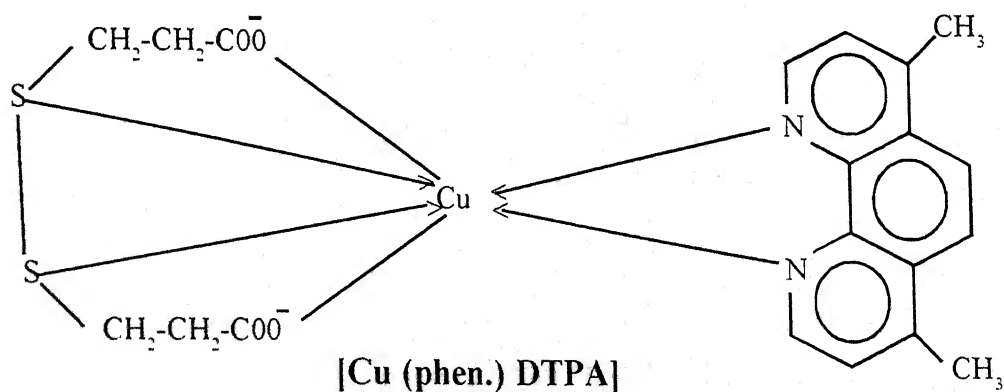
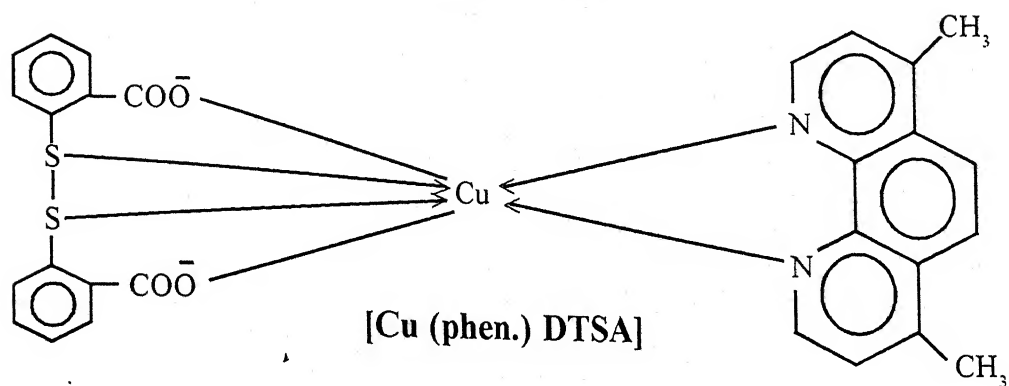
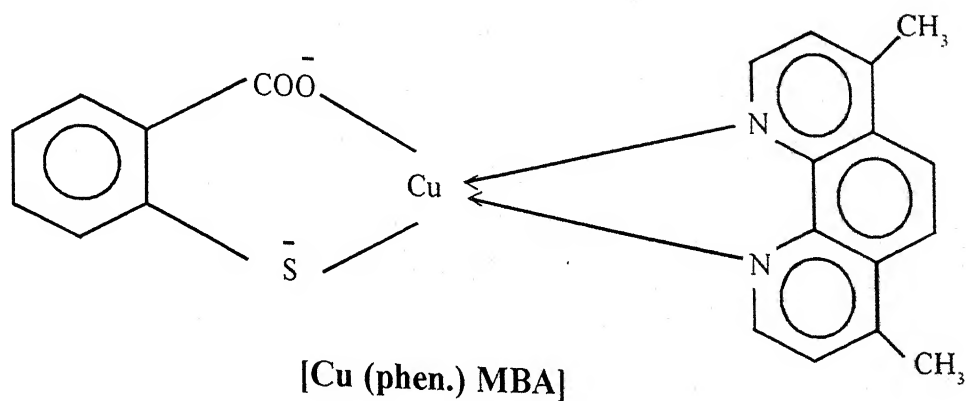


FIGURE 4.5

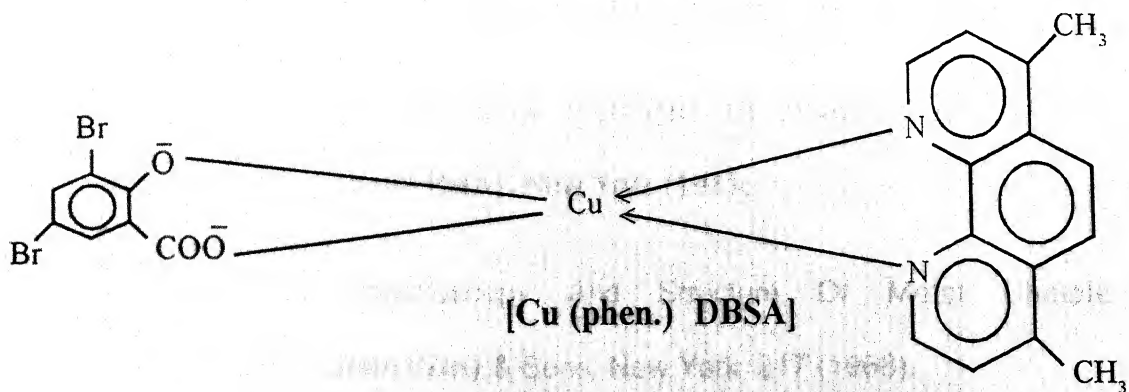
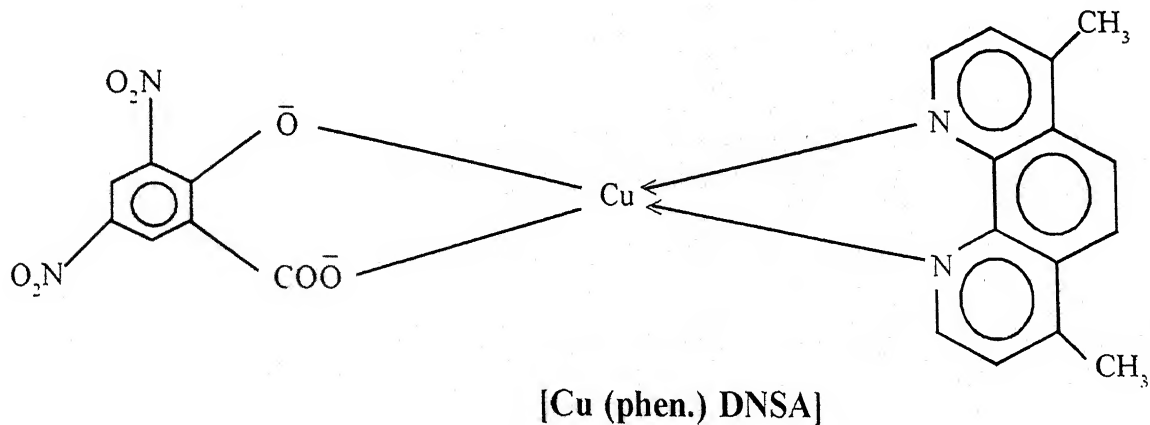
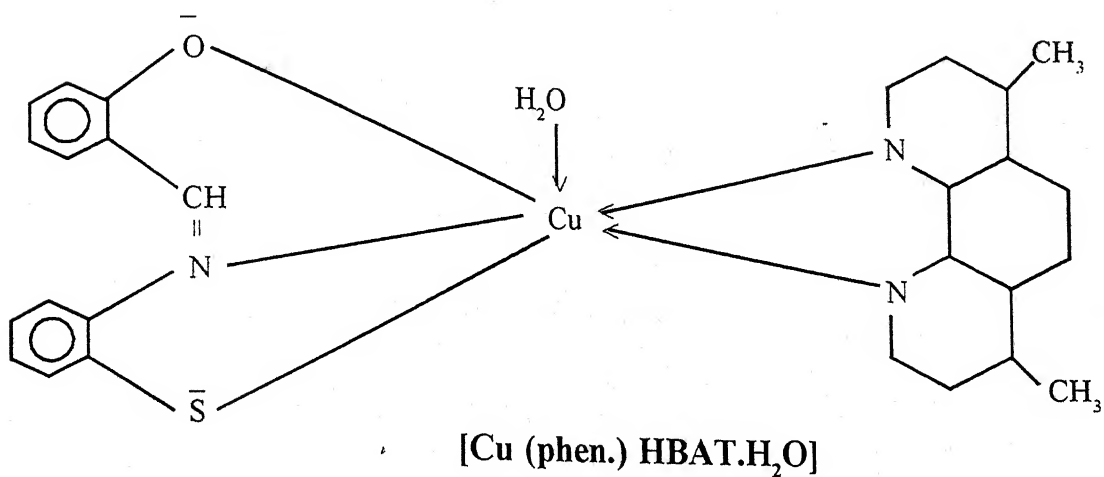
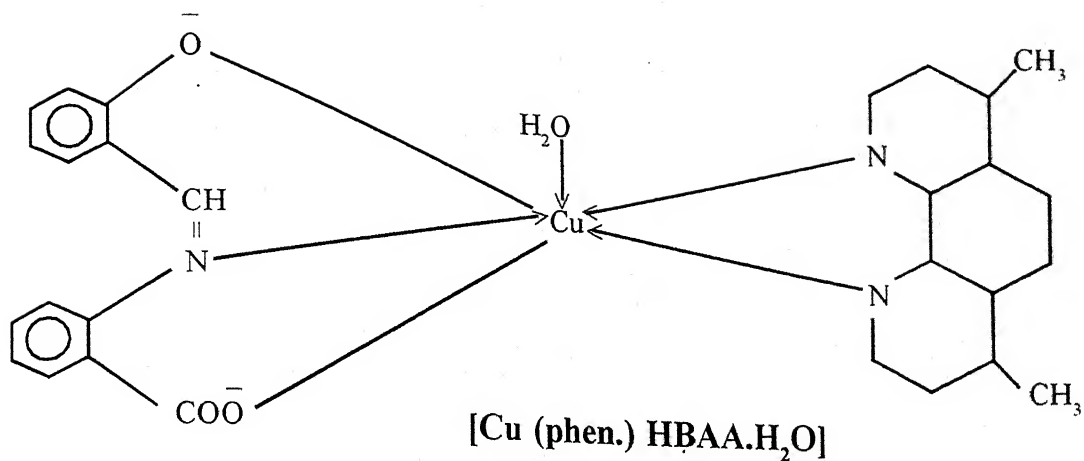


FIGURE 4.6

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CHAPTER - 5

CHAPTER - V

TERNARY COMPLEXES OF COBALT (II)

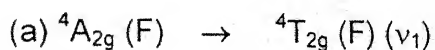
Results and Discussion

5.1 Electronic Spectra

We have already discussed the splitting of d energy levels in the four and six coordinate ligand fields and how the electronic transitions help us decide the geometry of the molecules of ternary complexes in the second chapter. The ternary complexes of Co (II) were also subjected to electronic spectral studies. The results are summarized in table 5.01.

The Co (II) ion has an electronic configuration of $3d^7$. It can form tetrahedral, square planar and octahedral complexes.

Three spectral bands in the region of $5920-17230\text{ cm}^{-1}$ have been observed for the Co (dipy.) complexes with MBA, DNSA, DBSA and HNA. The three bands correspond to the following transitions.



This is a definite indication of tetrahedral geometry of these four ternary complexes. The ratio ν_2/ν_1 is also found to fall in the range of 2.37 to 2.42 as required for tetrahedral complexes. Any remaining doubts about tetrahedral geometry are dispelled by the agreement of values of $10 Dq$, B and β with those expected for tetrahedral complexes.

TABLE 5.01

ELECTRONIC SPECTRAL DATA, THEIR ASSIGNMENTS AND LIGAND FIELD PARAMETERS OF Co (II) COMPLEXES

Compound	Observed Band Position (Cm ⁻¹)	Assignment	10 Dq. (Cm ⁻¹)	6 Dg. (Cm ⁻¹)	Racah Parameter (B)	Reduced % of B = $\frac{B \times 100}{B_0}$	Nephelauxetic Ratio (β) = $\frac{B}{B_0}$	% Covalent Character ($\beta\%$) = $1 - \beta \times 100$	LEFSE X Dq. 350 k cal/mole	v_2 / v_1
Co (dipy) TDPA. H ₂ O	8320	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
	15660	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7340	4404	593.34	52.97	0.5297	88.78	12.58	1.88
	18200	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	6080	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
Co (dipy) MBA	14456	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	8376	-	889.06	79.38	0.7938	25.97	28.71	2.37
	17120	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	8100	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
	15430	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7330	4398	708.66	63.27	0.6327	58.05	12.56	1.90
Co (dipy) TDAA. H ₂ O	19500	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	8016	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
	16220	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	8204	4922	769.73	68.72	0.6872	45.51	14.06	2.02
	19374	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
Co (dipy) DTSA	8210	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
	16110	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7900	4740	690.66	61.66	0.6166	62.17	13.54	1.96
	18880	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	8540	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
Co (dipy) PDA. H ₂ O	15990	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7450	4470	631.33	56.36	0.5636	77.43	12.77	1.87
	19100	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	8240	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
	15370	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7130	4278	611.66	54.61	0.5461	83.11	12.22	1.86
Co (dipy) HBAA. H ₂ O	18525	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								

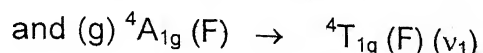
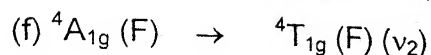
Table - 5.01 (Contd....)

[illegible]

Table - 5.01 (Contd....)

	8244	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
Co (phen) DNSA. 2H ₂ O	15896	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7652	4591	700.93	62.58	0.6258	59.79	13.11	1.92
	19350	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								
	8425	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F) [v_1]$								
Co (phen) DBSA. 2H ₂ O	15775	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) [v_2]$	7350	4410	692.00	61.78	0.6178	61.86	12.60	1.74
	19880	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P) [v_3]$								

The ternary complexes of MBA, HBA and DBSA with Co (II) (phen.) exhibit three bands in the range of 8425 cm^{-1} – 20360 cm^{-1} which may be assigned to the following transitions



These complexes, therefore, should have octahedral shape. Lower ν_2/ν_1 value of around 1.7 makes them distorted octahedral.

The rest of the ternary complexes of Co (bipy) and Co (phen.) too display three spectral bands in the regions $8016 - 8786\text{ cm}^{-1}$, $14456-16118\text{ cm}^{-1}$ and $18200-20140\text{ cm}^{-1}$ for the transition (e), (f) and (g) referred to above. Indeed the (f) transition in these complexes is so weak that it appears as a shoulder in the spectra of almost all these complexes. ν_2/ν_1 values in the range of 1.82 to 2.02 confirm their almost regular octahedral shape. The final confirmation of the stereochemistry is obtained from the $10 Dq$, $B\beta$ and LFSE values obtained for these ternary complexes.

5.2 Infra red studies

5.2.1. Co (dipy) ternary complexes

The infra red spectral frequencies of free ligands and ternary complexes along and their provision assignment for Co-phen systems have been summarized in table 5.02 to 5.11.

As already mentioned earlier, the IR spectra of the ligand undergoes significant changes. When it coordinates with a metal ion viz. Co (II) in this case.

TABLE - 5.02

IR SPECTRAL DATA OF dipy./TDPA LIGANDS AND THEIR COBALT COMPLEX

dipy.	TDPA	Co (dipy.) TDPA	Probable assignments
-	-	3430 (sb)	Coordinated H ₂ O mol.
-	2930 (m)	2915 (m)	Asym. CH ₂ -S Stretching.
-	2850 (s)	2830 (w)	Sym. CH ₂ -S Stretching.
-	1700 (s)	1680 (s)	Asym. C=O stretching.
1600 (s)	-	1570 (m)	C = N Stretching (Py.)
1585 (m)	-	1585 (m)	Aromatic C-C multiple band.
-	1440 (s)	1420 (s)	Sym. C = O Stretching.
-	1415 (m)	1400 (m)	CH ₂ -S deformation.
1410 (m)	-	1410 (m)	Aromatic C-C multiple band.
-	1360 (m)	1350 (m)	C = O Stretching.
1320 (w)	-	1300 (w)	C - N Stretching (Py.)
-	1250 (s)	1230 (m)	CH ₂ -S Wag.
1170 (w)	-	1165 (w)	Pyridine ring.
-	1050 (w)	1035 (w)	C - O Stretching.
-	920 (m)	-	OH deformation.
-	-	850 (wb)	Coordinated H ₂ O mol.
810 (s)	810 (s)	815 (wb)	Out of plane CH bending.
750 (w)	775 (m)	750 (m)	Out of plane CH bending.
740 (w)	760 (w)	755 (w)	Out of plane CH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
680 (w)	660 (s)	660 (m)	Out of plane CH deformation.
610 (wb)	-	615 (w)	Py. Ring deformation.
-	590 (w)	570 (m)	C.S. Stretching.
-	525 (m)	-	COOH Wagging mode.
-	-	460 (m)	M - O Stretching.
-	-	370 (m)	M - N Stretching.
-	-	300 (m)	M - S Stretching.

TABLE - 5.03

IR SPECTRAL DATA OF dipy./MBA LIGANDS AND THEIR COBALT COMPLEX

dipy.	MBA	Co (dipy.) MBA	Probable assignments
-	2590 (w)	-	S-H Stretching.
-	1660 (s)	1630 (sb)	Asym. C=O Stretching.
1600 (s)	-	1550 (m)	C=N Stretching (Py.)
1585 (m)	1600 (m)	-	Aromatic C-C multiple band.
1410 (m)	1460 (m)	1420 (s)	Aromatic-C-C multiple band.
-	1440 (m)	1410 (s)	Sym. C=O Stretching
1320 (w)	-	1300 (w)	C-N Stretching (Py.)
1170 (w)	-	1160 (m)	Pyridine ring.
-	1060 (w)	1070 (m)	Benzene breathing.
-	1050 (m)	1035 (w)	C=O Stretching.
-	920 (b)	-	OH deformation.
810 (s)	810 (m)	820 (m)	Out of plane CH bending.
750 (w)	-	760 (m)	Out of plane CH bending.
740 (w)	740 (ms)	740 (mb)	Out of plane CH bending.
680 (w)	660 (m)	665 (wb)	Out of plane CH deformation.
-	680 (m)	-	COOH bending.
610 (wb)	-	-	Pyridine ring deformation.
-	570 (m)	560 (wb)	C-S Stretching.
-	515 (w)	-	COOH Wagging mode.
-	-	460 (m)	M-O Stretching.
-	-	400 (m)	M-N Stretching.
-	-	320 (m)	M-S Stretching.

TABLE - 5.04

IR SPECTRAL DATA OF dipy./TDAA LIGANDS AND THEIR COBALT COMPLEX

dipy.	TDAA	Co (dipy.) TDAA	Probable assignments
-		3300 (m)	Coordinated H ₂ O mol.
-	2930 (s)	-	Asym. (CH ₂ -S) Stretching.
-	2850 (s)	-	Sym. (CH ₂ -S) Stretching.
-	1660 (s)	1630 (sb)	Asym. (C=O) stretching.
-	1400 (s)	1370 (s)	Sym. (C=O) Stretching.
1600 (s)	-	1580 (s)	C=N Stretching (Py.)
1585 (m)	-	-	Aromatic C-C multiple band.
1410 (m)	-	1410 (m)	Aromatic C-C multiple band.
-	1410 (m)	-	CH ₂ -S deformation.
1320 (w)	-	1300 (w)	C-N Stretching (Py.)
-	1225 (m)	1210 (s)	CH ₂ -S Wagging.
1170 (w)	-	1170 (w)	Pyridine ring.
-	-	1045 (m)	C=O Stretching.
-	920 (m)	-	OH deformation.
-	-	840 (mb)	Coordinated H ₂ O mol.
810 (s)	865 (m)	810 (m)	Out of plane CH bending.
750 (w)	825 (m)	770 (w)	Out of plane CH bending.
740 (w)	780 (w)	740 (sh)	Out of plane CH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
680 (w)	660 (s)	665 (m)	Out of plane CH deformation.
610 (wb)	-	630 (m)	Pyridine ring deformation.
-	570 (m)	550 (wb)	C-S Stretching.
-	-	480 (m)	M-O Stretching.
-	-	390 (m)	M-N Stretching.
-	-	290 (m)	M-S Stretching.

TABLE - 5.05

IR SPECTRAL DATA OF dipy./TDAA LIGANDS AND THEIR COBALT COMPLEX

dipy.	TDAA	Co (dipy.) TDAA	Probable assignments
-	1690 (s)	1620 (sb)	Asym. C=C Stretching.
1600 (s)	-	1525 (s)	C=N Stretching (Py.)
1585 (m)	1580 (m)	1575 (sh)	Aromatic C-C multiple band.
1410 (s)	1460 (m)	1465 (m)	Aromatic C-C multiple band.
-	1415 (s)	1360 (s)	Sym. C=O Stretching.
-	1360 (w)	-	C=O Stretching.
1320 (w)	-	1290 (w)	C=N Stretching.
1170 (w)	-	1165 (sh)	Pyridine ring.
-	1100 (w)	1095 (mb)	Benzene breathing.
-	910 (s)	-	OH deformation
810 (s)	800 (m)	810 (m)	Out of plane CH bending.
750 (w)	740 (s)	740 (s)	Out of plane CH bending.
740 (s)	-	-	Out of plane CH bending.
-	685 (m)	-	COOH bending.
680 (wb)	655 (m)	690 (m)	Out of plane CH deformation.
-	650 (m)	630 (m)	C-S Stretching.
610 (wb)	-	610 (wb)	Pyridine ring deformation.
-	555 (s)	-	COOH Wagging mode.
-	500 (w)	490 (mb)	S-S Stretching.
-	-	490 (m)	M-O Stretching.
-	-	450 (m)	M-N Stretching.
-	-	320 (m)	M-S Stretching.

TABLE - 5.06

IR SPECTRAL DATA OF dipy./DTPA LIGANDS AND THEIR COBALT COMPLEX

dipy.	DTPA	Co (dipy.) DTPA	Probable assignments
-	2930 (s)	2920 (m)	Asym. (CH ₂ -S) Stretching.
-	2850 (m)	2820 (m)	Sym. (CH ₂ -S) Stretching.
-	1690 (s)	1620 (sb)	Asym. (C=O) stretching.
1600 (s)	-	1550 (s)	C=N Stretching (Py.).
1585 (m)	-	1590 (m)	Aromatic C-C multiple band.
-	1440 (s)	1420 (s)	Sym. (C=O) Stretching.
1410 (s)	-	1415 (s)	Aromatic C-C multiple band.
-	1410 (s)	-	CH ₂ -S deformation.
1320 (w)	-	1285 (m)	C-N Stretching (Py.)
1170 (w)	-	1160 (w)	Py. ring.
-	1260 (s)	1230 (m)	CH ₂ -S Wagging.
-	1035 (w)	1030 (wm)	C-O Stretching.
-	920 (m)	-	OH deformation.
810 (s)	810 (m)	820 (m)	Out of plane CH bending.
750 (w)	-	-	Out of plane CH bending.
740 (w)	-	740 (w)	Out of plane CH bending.
680 (wb)	655 (m)	680 (mb)	Out of plane CH deformation.
-	660 (w)	630 (ms)	C-S Stretching.
610 (wb)	-	590 (wb)	Pyridine ring deformation.
-	550 (m)	-	COOH Wagging mode.
-	510 (m)	500 (mb)	S-S Stretching.
-	-	415 (m)	M-O Stretching.
-	-	395 (wm)	M-N Stretching.
-	-	300 (m)	M-S Stretching.

TABLE - 5.07

IR SPECTRAL DATA OF dipy./PDA LIGANDS AND THEIR COBALT COMPLEX

dipy.	PDA	Co (dipy.) PDA	Probable assignments
-	-	3450 (sb)	Coordinated H ₂ O mol.
-	1700 (s)	1640 (s)	Asym. C=O Stretching.
1600 (s)	1600 (wm)	1620 (m)	C=N Stretching (Py.)
1585 (m)	1580 (m)	1575 (s)	Aromatic C-C multiple band.
1410 (m)	1455 (m)	1455 (m)	Aromatic C-C multiple band.
-	1480 (m)	1440 (s)	Sym. C=O Stretching.
-	1350 (m)	1340 (m)	C-O Stretching.
1320 (w)	1310 (m)	1290 (m)	C-N Stretching (Py.)
-	1265 (m)	1250 (m)	C-N Stretching (Py.)
1170 (w)	1170 (m)	1165 (w)	Py. ring.
-	1035 (s)	1045 (m)	C-O Stretching.
-	910 (s)	-	OH deformation.
-	-	850 (wb)	Coordinated H ₂ O mol.
810 (s)	850 (w)	-	Out of plane CH bending.
750 (w)	745 (m)	750 (m)	Out of plane CH bending.
740 (w)	-	740 (m)	Out of plane CH bending.
-	690 (m)	-	COOH Wagging mode.
-	-	690 (mb)	Coordinated H ₂ O mol.
680 (wb)	650 (m)	685 (wm)	Out of plane CH deformation.
610 (wb)	600 (m)	610 (w)	Py. ring deformation.
-	520 (s)	-	COOH Wagging mode.
-	-	440 (m)	M-O Stretching.
-	-	350 (wm)	M-N Stretching.

TABLE - 5.08

IR SPECTRAL DATA OF dipy./HBAA LIGANDS AND THEIR COBALT COMPLEX

dipy.	HBAA	Co (dipy.) HBAA	Probable assignments
-	-	3410 (mb)	Coordinated H ₂ O mol.
-	3450 (sb)	-	OH phenolic Stretching.
-	1640 (s)	1600 (sm)	C=N Stretching (Azomethine).
-	1700 (s)	1620 (sb)	Asym. C=O Stretching.
1600 (s)	-	1590 (s)	C-N Stretching (Py.)
1585 (m)	1580 (m)	-	Aromatic C-C multiple band.
1410 (m)	-	-	Aromatic C-C multiple band.
-	1400 (m)	1385 (s)	Sym. C=O Stretching.
-	1370 (w)	1360 (wm)	C-O Stretching.
1320 (w)	-	1305 (w)	C-N Stretching (Py.)
-	1365 (m)	-	OH Phenolic bening.
-	1175 (m)	1160 (mw)	Phenolic CO Stretching.
1170 (w)	-	1160 (w)	Py. ring.
-	1080 (w)	1075 (w)	Benzene breathing.
-	930 (w)	-	OH deformation.
-	-	840 (wb)	Coordinated H ₂ O mol.
810 (s)	810 (m)	810 (m)	Out of plane CH bending.
750 (w)	755 (s)	755 (s)	Out of plane CH bending.
740 (w)	-	735 (w)	Out of plane CH bending.
-	690 (w)	-	COOH Wagging mode.
-	-	680 (mb)	Coordinated H ₂ O mol.
680 (wb)	675 (m)	675 (wb)	Out of plane CH deformation.
610 (wb)	-	600 (wb)	Py. ring deformation.
-	570 (wb)	-	COOH Wagging mode.
-	-	460 (wm)	M-O Stretching.
-	-	340 (wm)	M-N Stretching.

TABLE - 5.09

IR SPECTRAL DATA OF dipy./HBAT LIGANDS AND THEIR COBALT COMPLEX

dipy.	HBAT	Co (dipy.) HBAT	Probable assignments
-	-	3450 (sb)	Coordinated H ₂ O mol.
-	3250 (w)	-	OH phenolic Stretching.
-	2550 (w)	-	S=N Stretching (Azomethine).
-	1635 (s)	1615 (s)	C=N Stretching (Azomethine).
1600 (s)	-	1525 (s)	C-N Stretching (Py.)
1585 (m)	1580 (m)	1585 (m)	Aromatic C-C multiple band.
1410 (m)	1440 (s)	1445 (m)	Aromatic C-C multiple band.
-	1360 (m)	-	Ch phenolic bending.
1320 (w)	-	1305 (w)	C-N Stretching (Py.)
-	1175 (w)	1140 (m)	Phenolig CO Stretching.
1170 (w)	-	1170 (w)	Py. ring.
-	960 (w)	-	Benzene breathing.
-	-	820 (mb)	Coordinated H ₂ O mol.
810 (s)	880 (m)	-	Out of plane CH bending.
750 (w)	750 (s)	750 (wb)	Out of plane CH bending.
740 (w)	-	735 (sb)	Out of plane CH bending.
680 (wb)	695 (w)	685 (m)	Out of plane CH deformation.
-	-	690 (mb)	Coordinated H ₂ O mol.
-	660 (w)	620 (wm)	C-S stretching.
610 (wb)	-	600 (w)	Py. ring deformation.
-	-	420 (wm)	M-O Stretching.
-	-	405 (m)	M-N Stretching.
-	-	320 (m)	M-S Stretching.

TABLE - 5.10

IR SPECTRAL DATA OF dipy./DNSA LIGANDS AND THEIR COBALT COMPLEX

dipy.	DNSA	Co (dipy.) DNSA	Probable assignments
-	3490 (m)	-	OH phenolic Stretching.
-	1660 (s)	1640 (s)	Asym. C=O Stretching.
1585 (m)	1600 (m)	1585 (m)	Aromatic C-C multiple band.
1600 (s)	-	1540 (mb)	C=N Stretching (Py.)
-	1530 (s)	1530 (m)	Aromatic-NO ₂ group.
-	1440 (m)	1360 (s)	Sym. C=O Stretching.
1410 (m)	-	-	Aromatic C-C multiple band.
-	1380 (m)	1350 (m)	C-O Stretching.
-	1370 (m)	-	OH phenolic bending.
1320 (w)	1330 (m)	1300 (sh)	C-N Stretching.
-	1255 (s)	1290 (m)	C-N Stretching.
-	1170 (w)	1120 (wm)	Phenolic CO Stretching.
1170 (w)	-	1170 (w)	Py. ring.
-	1100 (w)	1095 (wm)	Benzene breathing.
-	1050 (w)	1040 (w)	C-O Stretching.
-	950 (w)	-	Benzene breathing.
-	930 (m)	-	OH deformation.
810 (s)	850 (mb)	815 (sb)	Out of plane CH bending.
750 (w)	740 (s)	-	Out of plane CH bending.
740 (w)	-	740 (m)	Out of plane CH bending.
680 (wb)	720 (m)	715 (m)	Out of plane CH deformation.
-	685 (m)	-	COOH bending.
610 (wb)	-	640 (m)	Py. ring deformation.
-	515 (wb)	-	COOH Wagging mode.
-	-	440 (wm)	M-O Stretching.
-	-	350 (m)	M-N Stretching.

TABLE - 5.11

IR SPECTRAL DATA OF dipy./DBSA LIGANDS AND THEIR COBALT COMPLEX

dipy.	DBSA	Co (dipy.) DBSA	Probable assignments
-	3240 (m)	-	OH phenolic Stretching.
-	1670 (sb)	1600 (s)	Asym. C=O Stretching.
1600 (s)	-	1540 (s)	C=N Stretching (Py.)
1585 (m)	1590 (m)	1610 (m)	Aromatic C-C multiple band.
1410 (s)	-	1415 (sh)	Aromatic C-C multiple band.
-	1420 (m)	1480 (mb)	Sym. C=O Stretching.
-	1380 (mb)	-	OH phenolic Stretching.
-	1350 (w)	1360 (wm)	C-O Stretching.
1320 (w)	-	1250 (m)	C=N Stretching (Py.)
-	1180 (w)	1120 (w)	Phenolic CO Stretching.
1170 (w)	-	1175 (m)	Py. ring.
-	1100 (w)	1105 (wm)	Benzene breathing.
-	910 (w)	-	OH deformation.
810 (s)	800 (mb)	810 (sb)	Out of plane CH bending.
750 (w)	780 (w)	-	Out of plane CH bending.
740 (w)	-	735 (m)	Out of plane CH bending.
680 (wb)	710 (m)	710 (m)	Out of plane CH deformation.
-	660 (wb)	-	Out of plane CH deformation.
-	685 (w)	-	COOH bending.
610 (wb)	-	625 (m)	Py. ring deformation.
-	600 (m)	600 (m)	C-Br. Stretching.
-	550 (w)	-	COOH Wagging mode.
-	470 (s)	475 (m)	C-Br. Stretching.
-	-	400 (m)	M-O Stretching.
-	-	390 (m)	M-N Stretching.

Thus, the spectral bands at 3450 cm^{-1} , 3490 cm^{-1} , 3240 cm^{-1} and 3450 cm^{-1} and also moderate ones characteristic of the stretching and bending phenolic OH groups in HBAA, HBAT, DNSA, DBSA and HNA free ligands respectively. It is significant when all these ligands separately form the ternary complexes with Co (II) along with (dipy), all these of bands vanish from the IR spectra. It is obvious that Co (II) to ligand bonding has taken place by replacing the proton in phenolic - OH group.

A significant lowering of symmetric and symmetric CH_2 stretching frequency by 930 cm^{-1} and 2850 cm^{-1} in TDPA, TDAA & DTPA to found to occur on complexation with the metal. Thus, the Co (II) (dipy) ternary complex should have coordination taking place with these ligands through the sulphur atom of the CH_2S group present.

Weak spectral bands at 2590 and 2550 cm^{-1} discussed for the free ligands MBA and HBAT respectively are attributed to S-H stretching vibration. It indicates that the SH group is deprotonated to form a covalent bond with Co (II) in the case of linear (bipy) complexes of these ligands.

It the case of all the free ligands forming ternary complexes with Co (bipy.), $\nu_{\text{as}}(\text{Co})$, $\nu_{\text{s}}(\text{Co})$ and $\nu_{\text{deform}}(\text{OH})$ are observed in the region of 1660 cm^{-1} form 1440 cm^{-1} , 1440 cm^{-1} and $920 \pm 10\text{ cm}^{-1}$. The is lowering of both carbonyl stretching frequencies in the range of 10 to 90 cm^{-1} and the third frequency completely vanished on complexation except for HBAA and DBSA in which case the sigmmeteric ν_{co} frequency shifts to a higher region by about 30 cm^{-1} . All

these ligands are, therefore, linked to the Co (II) through the carboxylic acid group.

The $\nu_{C=N}$ of a azomethine group in HBAA and HBA is observed as sharp spectral bands at 1640 cm^{-1} and 1635 cm^{-1} respectively. Here, too, there is lowering of the two frequencies by around 30 cm^{-1} . This lowering of frequency may be safely attributed to the coordination of each of the two ligands to metal through nitrogen atom of the a azomethine group¹⁻⁴.

Moderate spectral bands in the region of 1600 cm^{-1} are observed for $\nu_{C=N}$ vibrations of dipyrindine and PDA. This frequency too shift towards the negative direction on the complexation of the two ligands with Co (II). It indicates involvement of N of the pyridine ring in complex formation. Out of plane C-N bending and deformation frequency ($850\text{-}620\text{ cm}^{-1}$) and for the ring system ($1150\text{-}1000\text{ cm}^{-1}$) have been observed without exception in all cases⁷.

Moderate spectral bands attributed to ν_{C-S} vibrations for the TDPA, DTSA, DTPA and HBA in the region $610 \pm 50\text{ cm}^{-1}$ have observed. These vibrations also shift to a lower frequency by $10\text{-}40\text{ cm}^{-1}$ in Co-dipy. complexes to indicate that coordination has taken place through S atom of the C-S group.

Spectral bands at 500 cm^{-1} and 510 cm^{-1} respectively have been observed in free DTSA and DTPA. These bands are attributed to ν_{S-S} frequency. Lowering of this frequency by $10\text{-}30\text{ cm}^{-1}$ is indicative of coordination in these ligands coordinating through the 'S' atom.

The $\nu_{\text{Co-O}}$, $\nu_{\text{Co-N}}$ and $\nu_{\text{Co-S}}$ bands are found to appear in the region around $300\text{--}570\text{ cm}^{-1}$, $305\text{--}470\text{ cm}^{-1}$ and $260\text{--}3345\text{ cm}^{-1}$ respectively which confirms Co to O, Co-N and Co-S bond formation⁸⁻¹⁰.

In the dipy Co complexes of TDPA, TDAA, PDA, HBA, and HBAAT a broad band in the region of $3280\text{--}3500\text{ cm}^{-1}$ is observed. It is attributed to the stretching frequency of OH of the coordinated water molecule. The same complexes also exhibit moderate bands around $820\text{--}860\text{ cm}^{-1}$ and $680\text{--}690\text{ cm}^{-1}$. These bands are usually attributed to rocking and bending vibration respectively of CH group as noted by Nakamoto". When these complexes are heated in the temperature range of $120\text{--}180^{\circ}\text{C}$, there is negligible loss in their weight. This confirms that water molecules are not loosely held and are coordinated to Co (II).

On the contrary, in Co (dipy) DTSA and Co (dipy) DBSA complexes the presence of water is indicated by a broad spectral band at around 3450 cm^{-1} . But the corresponding bending and rocking vibration were not detectable in the expected range. Water molecules in these complexes, are therefore, not coordinated but held loose in their lattice".

Co (phen) – ternary complexes

The important infra red frequencies of 1 : 1 : 1 Co (phen) (carboxylic acid)/schiff's base) ternary complexes are listed in tables 5.13 to 5.19 along with comments on important peaks of the infra red spectra. There is a significant difference in position of important peaks of free ligands and their cobalt (II) complexes.

TABLE - 5.12

IR SPECTRAL DATA OF dipy./HNA LIGANDS AND THEIR COBALT COMPLEX

dipy.	HNA	Co (dipy.) HNA	Probable assignments
-	3450 (w)	-	OH phenolic Stretching.
-	1670 (sb)	1595 (s)	Asym. C=O Stretching.
1600 (s)	-	1615 (m)	C=N Stretching (Py.)
1585 (m)	1585 (m)	1585 (m)	Aromatic C-C multiple band.
-	1480 (mb)	1420 (mb)	Sym. C=O Stretching.
1410 (m)	-	1410 (m)	Aromatic C-c multiple band.
-	1380 (m)	1365 (m)	C-O Stretching.
-	1375 (mb)	-	OH phenolic bending.
1320 (w)	-	1290 (mb)	C-N Stretching (Py.)
-	1170 (m)	1220 (m)	Phenolic CO Stretching.
1170 (w)	-	1165 (m)	Py. ring.
-	1100 (w)	1095 (wm)	Benzene breathing.
-	1040 (w)	1025 (w)	C-O Stretching.
-	910 (w)	-	OH deformation.
810 (s)	800 (m)	810 (m)	Out of plane CH bending.
750 (w)	760 (w)	765 (m)	Out of plane CH bending.
740 (w)	-	745 (wm)	Out of plane CH bending.
-	685 (w)	-	COOH bending.
680 (wb)	660 (m)	660 (m)	Out of plane CH deformation.
610 (wb)	-	600 (w)	Py. ring deformation.
-	550 (m)	-	COOH Wagging mode.
-	-	430 (m)	M-O Stretching.
-	-	375 (mb)	M-N Stretching.

TABLE - 5.13

IR SPECTRAL DATA OF Phen./MBA LIGANDS AND THEIR COBALT COMPLEX

Phen.	MBA	Co (Phen.) MBA	Probable assignments
-	-	3450 (mb)	Coordinated H ₂ O mol.
-	2590 (m)	-	S-H stretching.
-	1690 (s)	1590 (m)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1570 (s)	Aromatic C-C multiple band.
1600 (s)	-	1520 (w)	C=N Stretching (Py.)
1500 (m)	1450 (m)	1440 (w)	Aromatic C-C multiple band.
-	1420 (m)	1400 (m)	Sym. C=O Stretching.
1340 (m)	-	1360 (m)	C-N Stretching (Py.)
1250 (s)	-	1250 (w)	C-N Stretching (Py.)
1165 (w)	-	1130 (m)	Py. ring.
1060 (w)	1060 (w)	-	Benzene breathing.
-	1050 (b)	1040 (w)	C-O Stretching.
-	930 (m)	-	O-H deformation.
-	-	850 (s)	Coordinated H ₂ O mol.
800 (s)	910 (m)	835 (m)	Out of plane CH bending.
770 (w)	740 (ms)	735 (w)	Out of plane CH bending.
-	-	690 (wb)	Coordinated H ₂ O mol.
665 (w)	660 (m)	690 (m)	Out of plane OH deformation.
-	680 (m)	-	COOH Wagging mode.
630 (w)	-	625 (m)	Py. ring deformation.
-	570 (m)	560 (w)	C-S Stretching.
-	520 (w)	-	COOH Wagging mode.
-	-	470 (m)	M-O Stretching.
-	-	410 (w)	M-N Stretching.
-	-	320 (m)	M-S Stretching.

TABLE - 5.14

IR SPECTRAL DATA OF Phen./DTSA LIGANDS AND THEIR COBALT COMPLEX

Phen.	DTSA	Co (Phen.) DTSA	Probable assignments
-	1680 (s)	1610 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1600 (m)	Aromatic C-C multiple band.
1600 (s)	-	1575 (s)	C=N Stretching (Py.)
1500 (m)	1480 (m)	1470 (m)	Aromatic C-C multiple band.
-	1415 (m)	1390 (w)	Asym. C=O Stretching.
-	1360 (m)	1340 (s)	C-O Stretching (Py.)
1340 (m)	-	-	C-N Stretching (Py.)
1250 (m)	-	1250 (w)	C-N Stretching (Py.)
1165 (s)	-	1130 (m)	Py. ring.
1060 (w)	1100 (w)	1060 (w)	Benzene breathing.
-	920 (s)	-	O-H deformation.
800 (s)	790 (m)	780 (s)	Out of plane CH bending.
770 (w)	730 (s)	735 (s)	Out of plane CH bending.
-	680 (m)	-	COOH bending.
665 (w)	650 (m)	670 (wb)	Out of plane CH deformation.
-	650 (m)	620 (m)	C-S Stretching.
630 (w)	-	615 (w)	Py. ring deformation.
-	555 (s)	-	COOH Wagging mode.
-	500 (w)	475 (mb)	S-S Stretching.
-	-	410 (m)	M-O Stretching.
-	-	330 (w)	M-N Stretching.
-	-	300 (m)	M-S Stretching.

TABLE - 5.15

IR SPECTRAL DATA OF Phen./PDA LIGANDS AND THEIR COBALT COMPLEX

Phen.	PDA	Co (Phen.) PDA	Probable assignments
-	-	3430 (sb)	Coordinated H ₂ O mol.
-	1700 (s)	1650 (sb)	Asym. C=O Stretching.
1670 (s)	1580 (m)	1560 (m)	Aromatic C-C multiple band.
1600 (m)	1600 (s)	1580 (m)	C=N Stretching (Py.)
1500 (s)	1460 (m)	1450 (s)	Aromatic C-C multiple band.
-	1420 (m)	1475 (m)	Sym. C=O Stretching.
-	1350 (s)	1365 (m)	C-O Stretching (Py.)
1340 (m)	1310 (w)	1280 (m)	C-N Stretching (Py.)
1250 (w)	1265 (s)	1220 (w)	C-N Stretching (Py.)
1165 (m)	1165 (m)	1160 (m)	Py. ring.
1060 (m)	-	1070 (m)	Benzene breathing.
-	1035 (m)	1025 (w)	C-O Stretching.
-	930 (m)	-	OH Stretching.
-	-	820 (wb)	Coordinated H ₂ O mol.
800 (s)	800 (s)	795 (m)	Out of plane CH bending.
770 (w)	740 (w)	770 (m)	Out of plane CH bending.
-	690 (m)	-	COOH bending.
-	-	690 (wb)	Coordinated H ₂ O mol.
665 (m)	650 (m)	665 (m)	Out of plane CH deformation.
630 (w)	600 (m)	640 (w)	Py. ring deformation.
-	520 (s)	-	COOH Wagging mode.
-	-	440 (mb)	M-O Stretching.
-	-	390 (m)	M-N Stretching.

TABLE - 5.16

IR SPECTRAL DATA OF Phen./HBAA LIGANDS AND THEIR COBALT COMPLEX

Phen.	HBAA	Co (Phen.) HBAA	Probable assignments
-	-	3420 (wb)	Coordinated H ₂ O mol.
-	3450 (w)	-	OH phenolic Stretching.
1670 (s)	-	-	Aromatic C-C multiple band.
-	1640 (s)	1590 (s)	C=N Stretching (Azomethine).
-	1620 (s)	1570 (m)	Asym. C=O Stretching.
1600 (m)	-	1530 (m)	C=N Stretching.
1500 (s)	1580 (m)	1510 (s)	Aromatic C-C multiple band.
-	1400 (m)	1370 (sb)	Sym. C=O Stretching.
-	1370 (w)	1350 (m)	C-O Stretching (Py.)
-	1365 (m)	-	OH phenolic bending.
1340 (m)	-	1300 (w)	C-N Stretching (Py.)
1250 (m)	-	1240 (w)	C-N Stretching (Py.)
-	1175 (w)	1135 (w)	Phenolic CO Stretching.
1165 (w)	-	1165 (m)	Py. ring.
1060 (w)	1070 (w)	1090 (s)	Benzene breathing.
-	925 (w)	-	OH deformation.
-	-	830 (mb)	Coordinated H ₂ O mol.
800 (s)	810 (m)	800 (m)	Out of plane CH bending.
770 (w)	755 (s)	760 (m)	Out of plane CH bending.
-	-	685 (wb)	Coordinated H ₂ O mol.
-	690 (w)	-	COOH bending.
665 (w)	675 (m)	660 (w)	Out of plane CH deformation.
630 (w)	-	640 (w)	Py. ring deformation.
-	570 (wb)	-	COOH Wagging mode.
-	-	450 (m)	M-O Stretching.
-	-	335 (m)	M-N Stretching.

TABLE - 5.17

IR SPECTRAL DATA OF Phen./HBAT LIGANDS AND THEIR COBALT COMPLEX

Phen.	HBAT	Co (Phen.) HBAT	Probable assignments
-	-	3420 (wb)	Coordinated H ₂ O mol.
-	3250 (m)	-	OH phenolic stretching.
-	2550 (w)	-	S-H Stretching.
1670 (m)	-	1665 (w)	Aromatic C-C multiple band.
-	1640 (s)	1600 (s)	C=N Stretching (Azomethine).
1600 (s)	-	1545 (m)	C=N Stretching (Py.)
1500 (m)	1580 (m)	1505 (s)	Aromatic C-C multiple band.
-	1440 (s)	1445 (s)	Aromatic C-C multiple band.
-	1360 (m)	-	OH phenolic stretching.
1340 (m)	-	1320 (wb)	C-N Stretching (Py.)
1250 (m)	-	1240 (w)	C-N Stretching (Py.)
-	1170 (w)	1150 (m)	Phenolic CO Stretching.
1165 (m)	-	1165 (m)	Py. ring.
1160 (w)	960 (m)	1050 (w)	Benzene breathing.
800 (s)	850 (w)	850 (m)	Out of plane CH bending.
-	-	830 (wb)	Coordinated H ₂ O mol.
770 (w)	740 (s)	745 (m)	Out of plane CH bending.
-	-	680 (m)	Coordinated H ₂ O mol.
665 (w)	690 (m)	-	Out of plane CH deformation.
-	660 (w)	630 (wb)	C-S Stretching.
630 (w)	-	620 (w)	Py. ring deformation.
-	-	420 (m)	M-O Stretching.
-	-	350 (m)	M-N Stretching.
-	-	290 (m)	M-S Stretching.

TABLE - 5.18

IR SPECTRAL DATA OF Phen./DNSA LIGANDS AND THEIR COBALT COMPLEX

Phen.	DNSA	Co (Phen.) DNSA	Probable assignments
-	-	3850 (mb)	Coordinated H ₂ O mol.
-	3490 (m)	-	OH phenolic stretching.
-	1680 (s)	1600 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	-	Aromatic C-C multiple band.
1600 (s)	-	1530 (s)	C=N Stretching (Py.)
1500 (m)	-	1485 (m)	Aromatic C-C multiple band.
-	1470 (s)	1460 (m)	Sym. C=O Stretching.
-	1380 (m)	1360 (s)	C-O Stretching (Py.)
-	1370 (m)	-	OH phenolic bending.
1340 (m)	1330 (m)	1310 (s)	C-N Stretching.
1250 (m)	1255 (b)	1190	C-N Stretching.
-	1175 (w)	1100	Phenolic CO Stretching.
1165 (m)	-	1160	Py. ring.
1060 (w)	1090 (w)	1070	Benzene breathing.
-	1050 (w)	-	C-O Stretching.
-	960 (w)	965	Benzene breathing.
-	930 (m)	-	OH deformation.
-	-	830	Coordinated H ₂ O mol.
800 (s)	840 (m)	830	Out of plane CH bending.
770 (w)	730 (m)	-	Out of plane CH bending.
665 (w)	715 (mb)	720	Out of plane CH deformation.
630 (w)	680 (s)	690	Py. ring deformation.
-	-	680	Coordinated H ₂ O mol.
-	515 (wb)	-	COOH Wagging mode.
-	-	410 (m)	M-O Stretching.
-	-	330 (w)	M-N Stretching.

TABLE - 5.19

IR SPECTRAL DATA OF Phen./DBSA LIGANDS AND THEIR COBALT COMPLEX

Phen.	DBSA	Co (Phen.) DBSA	Probable assignments
-	-	3490 (mb)	Coordinated H ₂ O mol.
-	3240 (w)	-	OH phenolic stretching.
-	1670 (sb)	1575 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1600 9s)	Aromatic C-C multiple band.
1600 (s)	-	1545 (s)	C=N Stretching (Py.)
1500 (m)	-	1500 (m)	Aromatic C-C multiple band.
-	1420 (mb)	1385 (mb)	Sym. C=O Stretching.
-	1380 (m)	-	OH phenolic bending.
-	1350 (w)	1300 (w)	C-O Stretching (Py.)
1340 (m)	-	-	C-N Stretching.
1250 (m)	-	1200 (m)	C-N Stretching.
-	1170 (w)	1150 (m)	Phenolic CO Stretching.
1165 (mb)	-	1160 (w)	Py. ring.
1060 (w)	1100 (w)	-	Benzene breathing.
-	915 (w)	-	OH deformation.
-	-	845 (m)	Coordinated H ₂ O mol.
800 (s)	860 (mb)	890 (s)	Out of plane CH bending.
770 (w)	770 (w)	780 (m)	Out of plane CH bending.
665 (w)	720 (w)	715 (mb)	Out of plane CH deformation.
-	-	680 (wb)	Coordinated H ₂ O mol.
-	660 (m)	650 (m)	Coordinated H ₂ O mol.
-	690 (m)	-	COOH bending.
630 (w)	-	630 (w)	Py. ring deformation.
-	600 (m)	605 (w)	C-Br Stretching.
-	550 (w)	-	COOH Wagging mode.
-	470 (s)	470 (mb)	C-Br Stretching.
-	-	430 (mb)	M-O Stretching.
-	-	310 (m)	M-N Stretching.

In the cobalt (phen) complexes with HBAA, HBAT, DNSA and DBSA, the bands corresponding to stretching and bending frequencies of – OH group present in the ligands disappear from their original positions at 3450 cm^{-1} , 3250 cm^{-1} , 3490 cm^{-1} and 3240 cm^{-1} in addition to those at 1365 cm^{-1} , 1360 cm^{-1} , 1370 cm^{-1} and 1380 cm^{-1} . This leads to conclusion that the proton from – OH group (phenolic) of the ligand has been replaced by cobalt (II).

The MBA and HBAT show spectral bands at 3590 cm^{-1} and 2550 cm^{-1} due to the S-H stretching vibrations. These band too disappear in the corresponding ternary complexes as in the case of phenolic –OH group. The conclusion is similar. The proton of the –SH group has been replaced by Co (II) ion to form M-S-C band.

The CO group in the free carboxylic acid ligand has bands at 1620 cm^{-1} , 1720 cm^{-1} and $1400\text{-}1425\text{ cm}^{-1}$ respectively corresponding to its symmetric and asymmetric stretching vibrations. The formation of a complex by such ligands with Co (phen) results in significant lowering of these frequencies in addition to total disappearance of –OH deformation (acid) seen at $920 \pm 10\text{ cm}^{-1}$. These ligands must have, therefore, linked to the metal through the carboxylic groups.

The C=N stretching vibration of a azomethine group in free HBAA and HBAT are manifest at 1640 cm^{-1} and 1635 cm^{-1} . However, in the Co (phen) ternary complexes there is a shift of $25\text{-}55\text{ cm}^{-1}$ towards the lower frequency region. This negative shifting in frequency indicated that N of azomethine group has coordinated with Co (II) to form the ternary complex.

The C=N stretching vibrations pyridine group present in (phen.) and PDA is exhibited as a sharp band around 1600 cm^{-1} . It too registers a negative shift of substantial proportions. Evidently N atom present in pyridine group is linking to Co (II) by a coordinate bond.

The band at 1165 cm^{-1} for the pyridine ring present in free (phen.) ligand overlaps with aromatic ring, C-C and C=C combination. This frequency is almost always lowered by $10\text{-}25\text{ cm}^{-1}$ in the ternary complexes of Co (phen). This is further confirmation of coordination of the ligand through N of the pyridine ring.

In Co (phen) DTSA ternary complex, the band at 500 cm^{-1} for S-S stretching vibration lowers by 30 cm^{-1} indicating the formation of Co-S bond in the complex¹².

In the ternary complexes of Co (phen) some bands in the region $395\text{-}480\text{ cm}^{-1}$ and $320\text{-}405\text{ cm}^{-1}$ may be assigned to $\nu_{\text{Co-O}}$ and $\nu_{\text{Co-N}}$ stretching vibration. Hence the ligands must have linked to the metal through HO and nitrogen atoms.

In the MBA, DBSA, PDA, HBAA, HBAT and DNSA complex with Co (phen), a broad band around $3410\text{-}3580\text{ cm}^{-1}$ is observed due to stretching vibration of OH of the coordinated water molecule. The rocking and bending vibration of -OH in the region $810\text{-}850\text{ cm}^{-1}$ and $680\text{-}690\text{ cm}^{-1}$ are further supportive of presence of coordinated water. That the water is coordinated and not present otherwise is confirmed by the heating of the corresponding ternary complex at $120\text{-}180^{\circ}\text{C}$. There is no loss of weight. Thus, there is no lattice water present.

5.3 Magnetic Studies

The effective magnetic moment values of the ternary complexes of cobalt, under study, have been listed in table 5.20.

On careful examination of the data in the table, it becomes clear the magnetic moment of all paramagnetic cobalt (II) complexes lies in the range of 3.80 to 5.37 B, M. It leads us to the conclusion that three unpaired electrons are present. Three unpaired electrons are possible if the ternary complex has spin free octahedral or a tetrahedral structure. The μ_{eff} value of all the cobalt (II) complexes barring Co (dipy) MBA, Co (dipy.) DNSA, Co (dipy) DBSA and Co (dipy.) HNA have been found to lie in the range of 4.02 to 5.37. They must possess spin free octahedral structure. The values of μ_{eff} are higher than calculated spin only values 3.87 B M on account orbital contribution to paramagnetism.

And for the four complexes listed as exceptions in the previous paragraph the μ_{eff} values are found to be 4.15, 4.13, 3.80 and 3.81 B.M. respectively. This is an indication of tetrahedral stereochemistry of the four complexes. The μ_{eff} values of DBSA and HNA ternary complexes are somewhat lower. This is probably due to lowering of symmetry. Perhaps negative orbital magnetic moment causes it. It leads us to conclude that Co (dipy) DBSA and Co (dipy) HNA complexes have a distorted tetrahedral geometry with sp^3 hybridization.

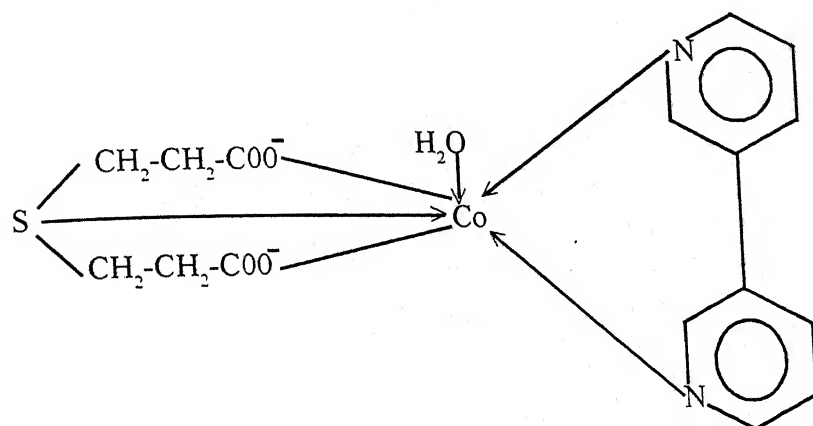
The bonding structural arrangements of in Cobalt (II) ternary complexes have been proposed and are represented in Fig. 5.1 to 5.5.

TABLE 5.20

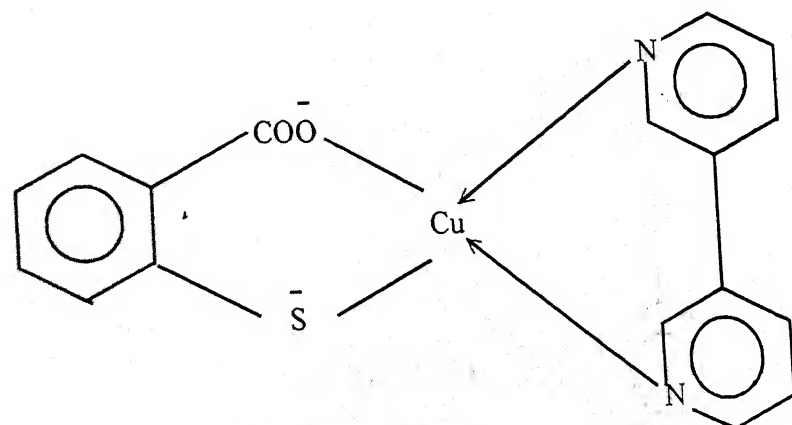
MAGNETIC MEASUREMENT DATA OF Co (II) COMPLEXES.

Compound	Molar susceptibility 'KM' = $K' \times M$ $\times 10^{-5}$	Diamagnetic correction (Dia) $\times 10^{-5}$	Corrected Molar susceptibility KM (Dia) $\times 10^{-5}$	Curie's value 'C' = KM (Dia) $\times T$ ($T=300+2^{\circ}K$) $\times 10^{-6}$	Magnetic susceptibility ' μ eff' = 2.84 C(BM)	Number of unpaired	Hybridization
Co (dipy) TDPA. H ₂ O	7937.9277	-206	8143.9277	2443178.3	4.44	3	Sp ³ d ²
Co (dipy) MBA	6987.7508	-184	7171.7508	2137181.7	4.15	3	Sp ³
Co (dipy) TDAA. H ₂ O	8711.8630	-182	8893.8630	2668158.9	4.63	3	Sp ³ d ²
Co (dipy) DTSA	8965.7483	-261	9226.7483	2786477.9	4.74	3	Sp ³ d ²
Co (dipy) DTPA	11818.9080	-210	12028.9080	3584614.5	5.37	3	Sp ³ d ²
Co (dipy) PDA. H ₂ O	7662.8867	-186	7848.8867	2338968.2	4.34	3	Sp ³ d ²
Co (dipy) HBAA. H ₂ O	9832.0277	-247	10079.0277	3003550.0	4.92	3	Sp ³ d ²
Co (dipy) HBAT. H ₂ O	10962.8880	-247	11209.8880	3340546.6	5.19	3	Sp ³ d ²
Co (dipy) DNSA	6836.3318	-183	7019.3318	2119838.2	4.13	3	Sp ³
Co (dipy) DBSA	5946.0037	-229	6175.0037	1852501.1	3.80	3	Sp ³
Co (dipy) HNA	5809.6738	-205	6014.6738	1804402.1	3.81	3	Sp ³
Co (phen) MBA. H ₂ O	6491.2123	-242	6733.2123	2006497.2	4.02	3	Sp ³ d ²
Co (phen) DTSA	11477.9580	-298	11775.9580	3509235.4	5.32	3	Sp ³ d ²
Co (phen) PDA. H ₂ O	8212.4568	-225	8437.4568	2514362.1	4.50	3	Sp ³ d ²
Co (phen) HBAA. H ₂ O	7047.0871	-285	7332.0871	2199626.1	4.21	3	Sp ³ d ²
Co (phen) HBAT. H ₂ O	9083.4248	-287	9370.4248	2811127.4	4.47	3	Sp ³ d ²
Co (phen) DNSA. 2H ₂ O	10662.3670	-254	10916.3670	3274910.1	5.13	3	Sp ³ d ²
Co (phen) DBSA. 2H ₂ O	9328.0857	-287	9615.0957	2884525.7	4.82	3	Sp ³ d ²

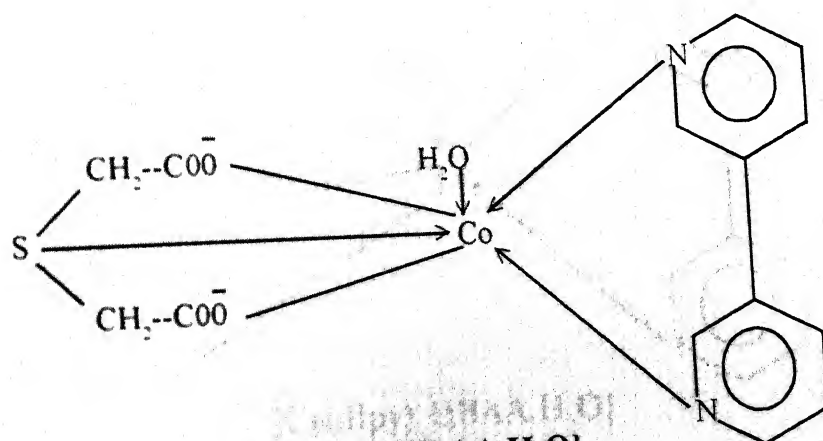
PROPOSED BONDING STRUCTURES OF DIPYRIDINE COBALT (II) COMPLEXES



[Co(dipy) TDPA.H₂O]



[Co(dipy) MBA]



[Co(dipy) TDAA.H₂O]

FIGURE 5.1

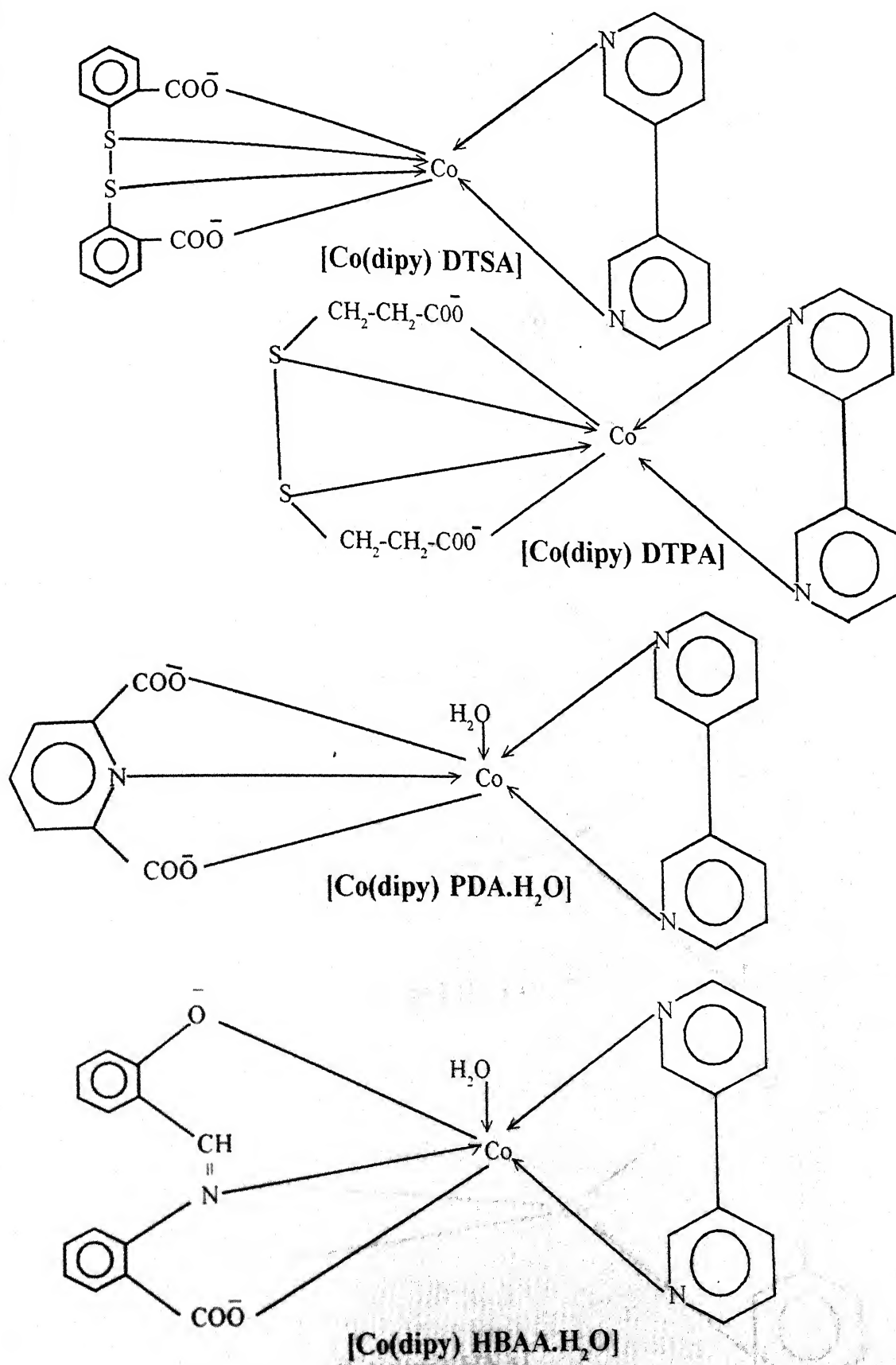


FIGURE 5.2

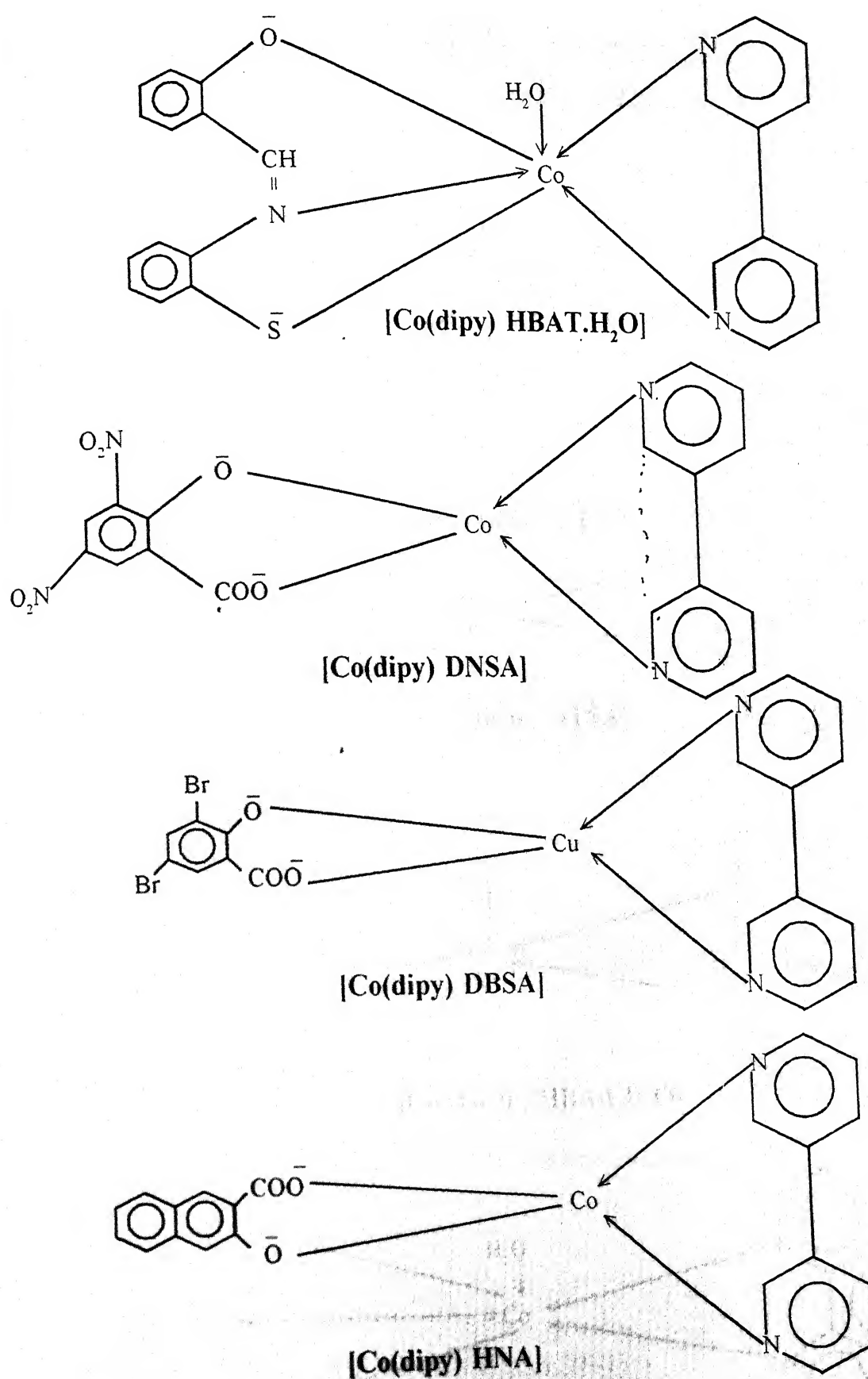


FIGURE 5.3

PROPOSED BONDING STRUCTURES OF PHENANTHROLINE COBALT (II) COMPLEXES

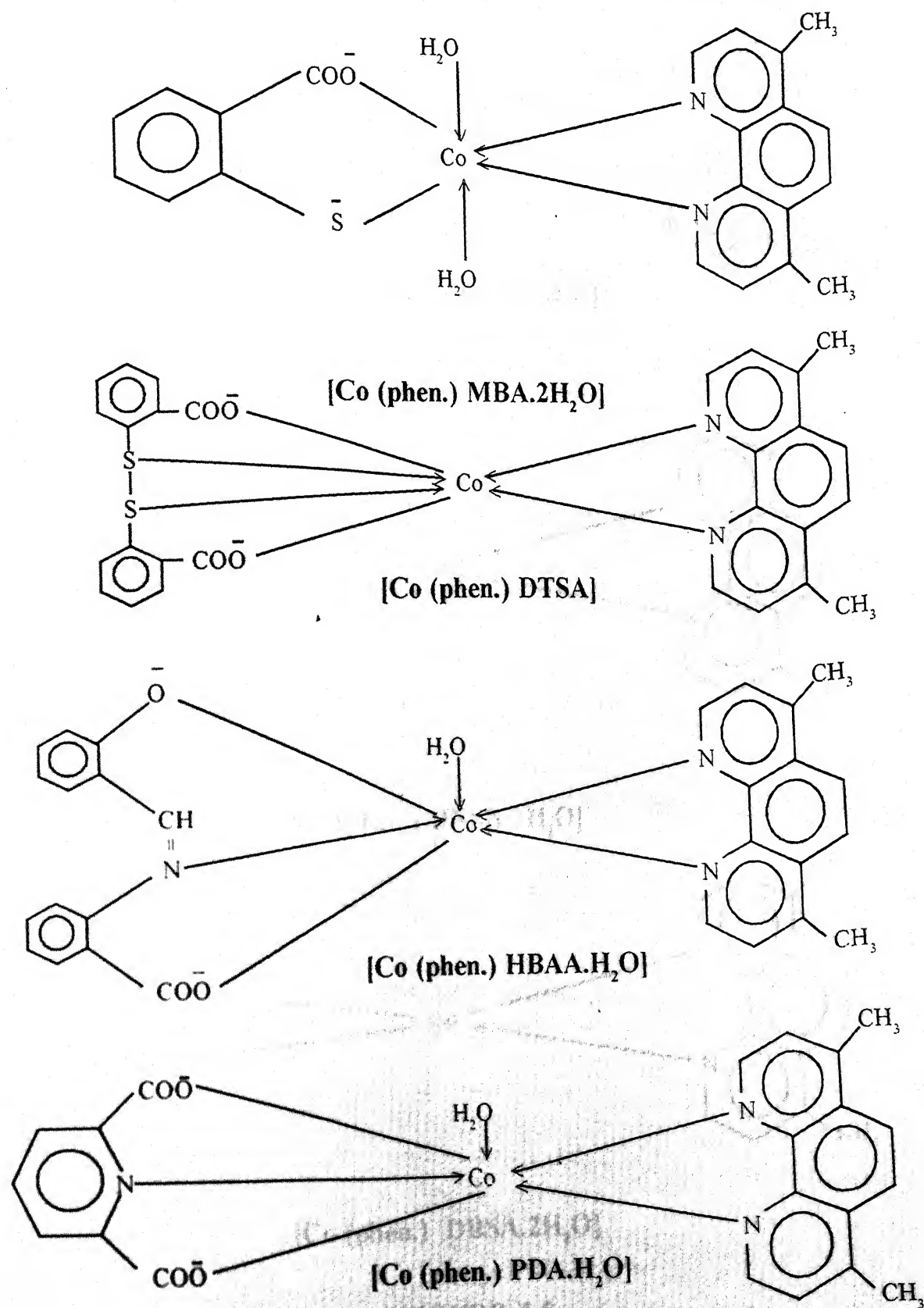


FIGURE 5.4

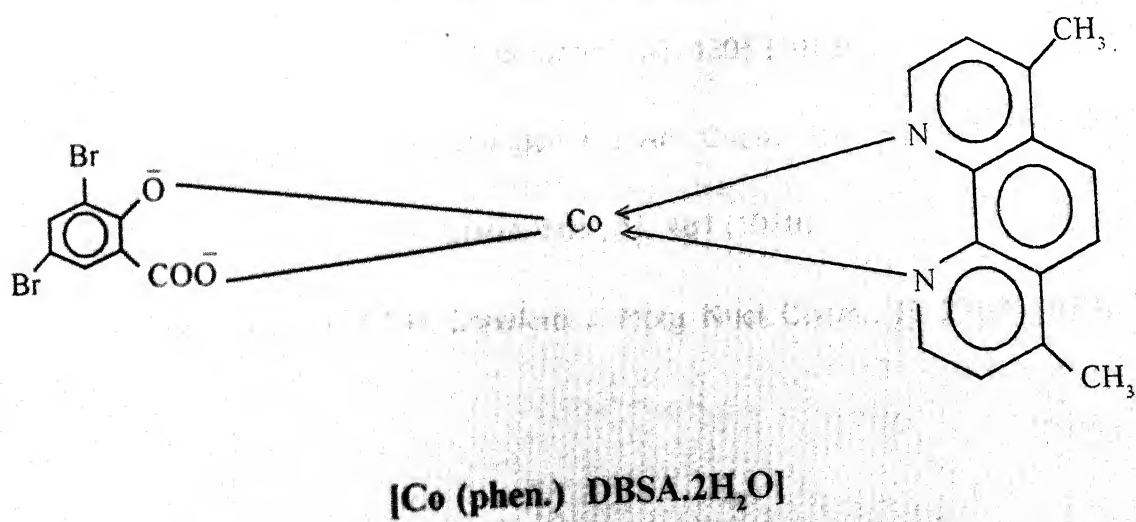
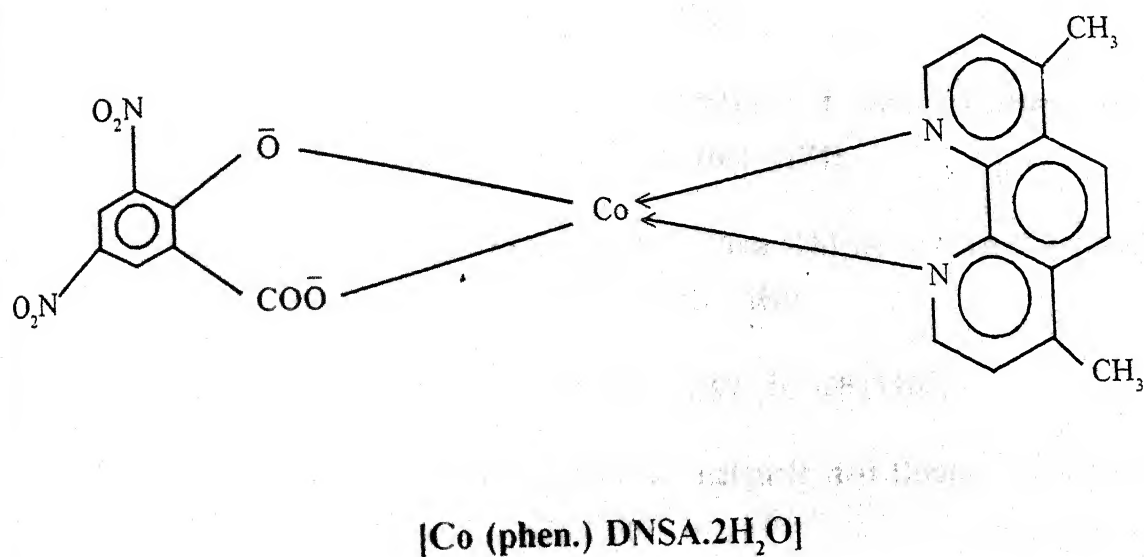
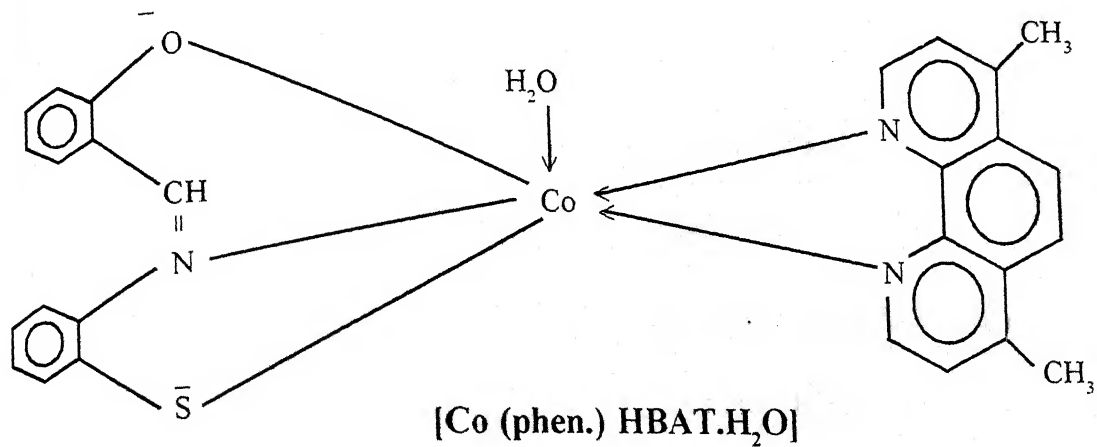


FIGURE 5.5

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CHAPTER - 6

CHAPTER - VI

TERNARY COMPLEXES OF NICKEL (II)

Results and Discussion

6.1 Electronic Spectral Studies

The electronic spectral data of nickel (II) ternary complexes are listed in table 6.01.

Nickel (II), as we know, has shown ample ability to form coordination complexes. In the complexes, there is a large crystal field splitting, no transition occurs below 10000 cm^{-1} in the case of low spin square planar complexes. This is evidently so on account of the energy difference between $d_{x^2-y^2}$ and the next lower level being greater than 10 KK .

The Ni (dipy.) MBA, Ni (dipy.) DNSA, Ni (dipy.) HNA and Ni (phen.) MBA complexes exhibit electronic bands in the $18130\text{-}18620\text{ cm}^{-1}$, $28790\text{-}29900\text{ cm}^{-1}$ and $34170\text{-}35170\text{ cm}^{-1}$ corresponding to the transitions $^1A_{1g} \rightarrow ^1E_u$ (ν_1), $^1A_{1g} \rightarrow ^1A_{2u}$ (ν_2) and $^1A_{1g} \rightarrow ^1B_u$ (ν_3) respectively. These complexes can be therefore, assumed to possess square planar geometry. The B , β and ν_2/ν_1 values support this assumption with a partial covalent character in the metal – ligand bond as β values lie in the range of 0.55 to 0.59 .

A spectral band below 10 KK and remaining two bands around 15000 and 19000 cm^{-1} are due to $^3T_1 \rightarrow ^3A_2$, $^3T_1 \rightarrow ^3T_2$ and $^3T_1 \rightarrow ^3T_1$ (P) transitions respectively for tetrahedral complexes of Ni (II)¹. The Ni (dipy.) DBSH and Ni

TABLE 6.01

ELECTRONIC SPECTRAL DATA, THEIR ASSIGNMENTS AND LIGAND FIELD PARAMETERS OF Ni (II) COMPLEXES

Compound	Observed Band Position (cm ⁻¹)	Assignment	10 Dq. (cm ⁻¹)	6 Dg. (dm ⁻¹)	Racah parameter (B)	Reduced % of B = $\frac{B \times 100}{B_0}$ (B ₀ =1080)	Nephelauxetic Ratio (β) = $\frac{B}{B_0}$	% Covalent Character (β%) = $\frac{1-\beta \times 100}{\beta}$	LEFSE = $\frac{X \text{ Dq.}}{350}$ k cal/mole	v ₂ / v ₁
Ni (dipy) TDPA. H ₂ O	10690	³ A _{2g} → ³ T _{2g} (P) [v ₁]								
	19870	³ A _{2g} → ³ T _{1g} [v ₂]	10690	-	682.00	63.14	0.6314	58.37	36.65	1.85
	22430	³ A _{2g} → ³ T _{2g} (P) [v ₃]								
	18200	¹ A _{1g} → ¹ E _u [v ₁]								
	29520	¹ A _{1g} → ¹ A _{2u} [v ₂]	18200	-	638.66	59.13	0.5913	69.11	-	1.62
Ni (dipy) MBA	34660	¹ A _{1g} → ¹ B _{1u} [v ₃]								
	9520	³ A _{2g} → ³ T _{2g} [v ₁]								
	17900	³ A _{2g} → ³ T _{1g} [v ₂]	9520	-	664.00	61.48	0.6148	62.65	32.64	1.88
	20620	³ A _{2g} → ³ T _{1g} (P) [v ₃]								
	10230	³ A _{2g} → ³ T _{2g} [v ₁]								
Ni (dipy) DTSA	18950	³ A _{2g} → ³ T _{1g} [v ₂]	10230	-	684.66	63.39	0.6339	57.75	35.07	1.85
	22010	³ A _{2g} → ³ T _{1g} (P) [v ₃]								
	9980	³ A _{2g} → ³ T _{2g} [v ₁]								
	18740	³ A _{2g} → ³ T _{1g} [v ₂]	9980	-	633.33	61.41	0.6141	62.83	34.21	1.87
	21150	³ A _{2g} → ³ T _{1g} (P) [v ₃]								

Table - 6.01 (Contd...)

Ni (dipy) PDA H ₂ O	11870	$^3A_{2g} \rightarrow ^3T_{2g}$	[v ₁]	11870	-	705.33	65.30	0.6530	53.13	40.69	1.67
	19890	$^3A_{2g} \rightarrow ^3T_{1g}$	[v ₂]								
	26300	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	[v ₃]								
	8980	$^3A_{2g} \rightarrow ^3T_{2g}$	[v ₁]								
Ni (dipy) HBAA H ₂ O	17240	$^3A_{2g} \rightarrow ^3T_{1g}$	[v ₂]	8980	-	713.33	66.04	0.6604	51.42	30.78	1.91
	20400	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	[v ₃]								
	9250	$^3A_{2g} \rightarrow ^3T_{2g}$	[v ₁]								
Ni (dipy) HBAT H ₂ O	17540	$^3A_{2g} \rightarrow ^3T_{1g}$	[v ₂]	2950	-	670.03	62.03	0.6203	61.21	31.71	1.89
	20260	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	[v ₃]								
	18130	$^1A_{1g} \rightarrow ^1E_u$	[v ₁]								
Ni (dipy) DNSA	28790	$^1A_{1g} \rightarrow ^1A_{2u}$	[v ₂]	18130	-	633.33	58.64	0.5864	70.53	-	1.58
	35100	$^1A_{1g} \rightarrow ^1B_u$	[v ₃]								
	8470	$^3T_1 \rightarrow ^3A_2$	[v ₁]								
Ni (dipy) DBSA	15560	$^3T_1 \rightarrow ^3T_2$	[v ₂]	8470	5082	645.33	59.75	0.5975	67.36	14.52	1.83
	19530	$^3T_1 \rightarrow ^3T_1 (P)$	[v ₃]								
	18300	$^1A_{1g} \rightarrow ^1E_u$	[v ₁]								
Ni (dipy) HNA	29780	$^1A_{1g} \rightarrow ^1A_{2u}$	[v ₂]	18300	-	603.33	55.86	0.5586	79.01	-	1.62
	34170	$^1A_{1g} \rightarrow ^1B_u$	[v ₃]								
	9500	$^3A_{2g} \rightarrow ^3T_{2g}$	[v ₁]								
Ni (dipy) DPDC H ₂ O	17300	$^3A_{2g} \rightarrow ^3T_{1g}$	[v ₂]	9500	-	694.00	64.25	0.6425	55.64	32.57	1.82
	21610	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	[v ₃]								
	18620	$^1A_{1g} \rightarrow ^1E_u$	[v ₁]								
Ni (phen) MBA	29900	$^1A_{1g} \rightarrow ^1A_{2u}$	[v ₂]	18620	-	614.00	56.85	0.5685	75.90	-	1.60
	35170	$^1A_{1g} \rightarrow ^1B_u$	[v ₃]								

Table - 6.01 (Contd....)

Ni (phen) DTSA	10120	${}^3A_{2g} \rightarrow {}^3T_{2g}$ [ν_1]	10120	-	664.66	61.54	0.6154	62.49	34.69	1.66
	16830	${}^3A_{2g} \rightarrow {}^3T_{1g}$ [ν_2]								
	23500	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [ν_3]								
	8760	${}^3A_{2g} \rightarrow {}^3T_{2g}$ [ν_1]								
Ni (phen) PDA. H ₂ O	16680	${}^3A_{2g} \rightarrow {}^3T_{1g}$ [ν_2]	8760	-	700.00	64.81	0.6481	54.29	30.03	1.90
	20100	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [ν_3]								
	12680	${}^3A_{2g} \rightarrow {}^3T_{2g}$ [ν_1]								
Ni (phen) HBAA. H ₂ O	20890	${}^3A_{2g} \rightarrow {}^3T_{1g}$ [ν_2]	12680	-	694.00	64.25	0.6425	55.64	43.47	1.64
	27560	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [ν_3]		-						
	11530	${}^3A_{2g} \rightarrow {}^3T_{2g}$ [ν_1]								
Ni (phen) HBAT. H ₂ O	20980	${}^3A_{2g} \rightarrow {}^3T_{1g}$ [ν_2]	11530	-	694.00	64.25	0.6425	55.64	39.59	1.81
	24020	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [ν_3]								
	8650	${}^3T_1 \rightarrow {}^3A_2$ [ν_1]								
Ni (phen) DNSA	15340	${}^3T_1 \rightarrow {}^3T_2$ [ν_2]	8650	5190	603.33	55.86	0.5586	79.01	14.82	1.77
	19660	${}^3T_1 \rightarrow {}^3T_1 (P)$ [ν_3]								
	9750	${}^3A_{2g} \rightarrow {}^3T_{2g}$ [ν_1]								
Ni (phen) DBSA. 2H ₂ O	16440	${}^3A_{2g} \rightarrow {}^3T_{1g}$ [ν_2]	9750	-	686.00	63.51	0.6351	57.45	33.42	1.68
	23100	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ [ν_3]								

(phen.) DNSA complexes do exhibit these transitions at $8470 - 8650 \text{ cm}^{-1}$, $15340-15560 \text{ cm}^{-1}$ and $19530-196600 \text{ cm}^{-1}$. The two complexes are, therefore, expected to possess tetrahedral geometry. The 10 Dg. B, β , LFSE and v_2/v_1 values also confirm the contention.

All the remaining nickel (II) complexes exhibit three spin allowed transitions $^3A_{2g} \rightarrow ^3T_{2g} (P) (v_1)$, $^3A_{2g} \rightarrow ^3T_{1g} (v_2)$ and $^3A_{2g} \rightarrow ^3T_{1g} (P) (v_3)$, in the range of $18760-12680 \text{ cm}^{-1}$, $16440-20980 \text{ cm}^{-1}$ and $20100-27500 \text{ cm}^{-1}$ respectively. It leads us to the conclusion that all these complexes are octahedrally surrounded by ligands. In fact, the 10 Dg values, B, β , LFSE and v_2/v_1 values render their support to this conclusion except in the case of Ni (dipy.) PDA, Ni (phen.) DTSA, Ni (phen.) HBAA and Ni (dipy.) DBSA in which lower values of v_2/v_1 (1.64-1.68) are suggestive of distorted octahedral structure.

6.2. Infra Red Studies

6.2.1. Ni (dipy.) ternary complexes

The IR spectral data for the complexes, under investigation is in listed in tables 6.02 to 6.13.

The vibrational spectra of nickel (II) dipyrindine complexes with different ligands are quite similar to those obtained for similar complexes of cobalt (II) and Copper (II).

One notable deviation was observed for Ni (dipy.) TDPA wherein the asymmetric and symmetric $\text{CH}_2\text{-S}$ vibration frequencies shift to a higher region by $20-30 \text{ cm}^{-1}$ instead of shifting to a lower region as in other complexes of

TABLE - 6.02

IR SPECTRAL DATA OF dipy./TDPA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	TDPA	Ni (dipy.) TDPA	Probable assignments
-	-	3460 (s)	Coordinated H ₂ O mol.
-	2930 (m)	2960 (m)	Asym. CH ₂ -S Stretching.
-	2850 (s)	2860 (w)	Sym. CH ₂ -S Stretching.
-	1700 (s)	1690 (m)	Asym. C=O stretching.
1600 (s)	-	1590 (m)	C = N Stretching (Py.)
1585 (m)	-	1580 (s)	Aromatic C-C multiple band.
-	1440 (s)	1410 (m)	Sym. C = O Stretching.
-	1415 (m)	1405 (m)	CH ₂ -S deformation.
1410 (m)	-	1410 (w)	Aromatic C-C multiple band.
-	1360 (m)	1340 (m)	C = O Stretching.
1320 (w)	-	1305 (w)	C - N Stretching (Py.)
-	1250 (s)	1235 (m)	CH ₂ -S Wag.
1170 (w)	-	1165 (w)	Pyridine ring.
-	1050 (w)	1075 (w)	C - O Stretching.
-	920 (m)	-	OH deformation.
-	-	820 (wb)	Coordinated H ₂ O mol.
810 (s)	810 (w)	810 (mb)	Out of plane CH bending.
750 (w)	775 (m)	760 (w)	Out of plane CH bending.
740 (w)	760 (w)	-	Out of plane CH bending.
-	-	685 (mb)	Coordinated H ₂ O mol.
680 (w)	660 (s)	670 (m)	Out of plane CH deformation.
610 (wb)	-	615 (w)	Py. Ring deformation.
-	590 (w)	550 (wb)	C.S. Stretching.
-	525 (m)	-	COOH Wagging mode.
-	-	400 (m)	M - O Stretching.
-	-	350 (w)	M - N Stretching.
-	-	310 (m)	M - S Stretching.

TABLE - 6.03

IR SPECTRAL DATA OF dipy./MBA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	MBA	Ni (dipy.) MBA	Probable assignments
-	2590 (w)	-	S-H Stretching.
-	1660 (s)	1615 (s)	Asym. C=O Stretching.
1600 (s)	-	1560 (s)	C=N Stretching (Py.)
1585 (m)	1600 (m)	1590 (w)	Aromatic C-C multiple band.
1410 (m)	1460 (m)	1410 (m)	Aromatic C-C multiple band.
-	1440 (m)	1395 (s)	Sym. C=O Stretching
1320 (w)	-	1305 (w)	C-N Stretching (Py.)
1170 (w)	-	1105 (w)	Pyridine ring.
-	1060 (w)	1065 (w)	Benzene breathing.
-	1050 (m)	1040 (m)	C=O Stretching.
-	920 (b)	-	OH deformation.
810 (s)	810 (m)	815 (m)	Out of plane CH bending.
750 (w)	-	750 (mb)	Out of plane CH bending.
740 (w)	740 (ms)	735 (w)	Out of plane CH bending.
680 (w)	660 (m)	660 (w)	Out of plane CH deformation.
-	680 (m)	-	COOH bending.
610 (wb)	-	600 (wb)	Pyridine ring deformation.
-	570 (m)	540 (m)	C-S Stretching.
-	515 (w)	-	COOH Wagging mode.
-	-	440 (m)	M-O Stretching.
-	-	380 (m)	M-N Stretching.
-	-	290 (m)	M-S Stretching.

TABLE - 6.04

IR SPECTRAL DATA OF dipy./TDAA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	TDAA	Ni (dipy.) TDAA	Probable assignments
-	-	3300 (s)	Coordinated H ₂ O mol.
-	2930 (s)	2900 (w)	Asym. (CH ₂ -S) Stretching.
-	2850 (s)	2830 (m)	Sym. (CH ₂ -S) Stretching.
-	1660 (s)	1595 (s)	Asym. (C=O) stretching.
-	1400 (s)	1350 (s)	Sym. (C=O) Stretching.
1600 (s)	-	1570 (m)	C=N Stretching (Py.)
1585 (m)	-	1580 (m)	Aromatic C-C multiple band.
1410 (s)	-	-	Aromatic C-C multiple band.
-	1410 (m)	1370 (s)	CH ₂ -S deformation.
1320 (w)	-	1285 (w)	C-N Stretching (Py.)
-	1225 (m)	1240 (wm)	CH ₂ -S Wagging.
1170 (w)	-	1165 (w)	Pyridine ring.
-	-	1050 (m)	C-O Stretching.
-	920 (m)	-	OH - deformation.
-	-	825 (wb)	Coordinated H ₂ O mol.
810 (s)	865 (m)	815 (m)	Out of plane CH bending.
750 (w)	825 (m)	755 (m)	Out of plane CH bending.
740 (w)	780 (w)	720 (m)	Out of plane CH bending.
-	-	685 (mb)	Coordinated H ₂ O mol.
680 (wb)	660 (s)	700 (m)	Out of plane CH deformation.
610 (wb)	-	620 (w)	Py. ring deformation.
-	570 (m)	565 (w)	C-S Stretching.
-	-	400 (m)	M-O Stretching.
-	-	370 (w)	M-N Stretching.
-	-	260 (m)	M-S Stretching.

TABLE - 6.05

IR SPECTRAL DATA OF dipy./DTSA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	DTSA	Ni (dipy.) DTSA	Probable assignments
-	1690 (s)	1615 (s)	Asym. C=C Stretching.
1600 (s)	-	1535 (s)	C=N Stretching (Py.)
1585 (m)	1580 (m)	1585 (w)	Aromatic C-C multiple band.
1410 (s)	1460 (m)	1405 (m)	Aromatic C-C multiple band.
-	1415 (s)	1390 (sb)	Sym. C=O Stretching.
-	1360 (w)	1285 (w)	C-O Stretching.
1320 (w)	-	1250 (w)	C-N Stretching.
1170 (w)	-	1160 (w)	Pyridine ring.
-	1100 (w)	-	Benzene breathing.
-	910 (s)	-	OH deformation
810 (s)	800 (m)	810 (m)	Out of plane CH bending.
750 (w)	740 (s)	755 (m)	Out of plane CH bending.
740 (s)	-	-	Out of plane CH bending.
-	685 (m)	-	COOH bending.
680 (wb)	655 (m)	670 (m)	Out of plane CH deformation.
-	650 (m)	560 (m)	C-S Stretching.
610 (wb)	-	-	Py. ring deformation.
-	555 (s)	-	COOH Wagging mode.
-	500 (w)	425 (w)	S-S Stretching.
-	-	450 (m)	M-O Stretching.
-	-	410 (w)	M-N Stretching.
-	-	300 (m)	M-S Stretching.

TABLE - 6.06

IR SPECTRAL DATA OF dipy./DTPA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	DTPA	Ni (dipy.) DTPA	Probable assignments
-	2930 (s)	2915 (s)	Asym. (CH ₂ -S) Stretching.
-	2850 (m)	2760 (w)	Sym. (CH ₂ -S) Stretching.
-	1690 (s)	1660 (m)	Asym. (C=O) stretching.
1600 (s)	-	1590 (s)	C=N Stretching (Py.).
1585 (m)	-	1585 (m)	Aromatic C-C multiple band.
-	1440 (s)	1400 (s)	Sym. (C=O) Stretching.
1410 (s)	-	-	Aromatic C-C multiple band.
-	1410 (s)	1395 (w)	CH ₂ -S deformation.
1320 (w)	-	1310 (m)	C-N Stretching (Py.)
1170 (w)	-	1150 (m)	Py. ring.
-	1260 (s)	1235 (m)	CH ₂ -S Wagging.
-	1035 (w)	1040 (m)	C-O Stretching.
-	920 (m)	-	OH deformation.
810 (s)	810 (m)	810 (m)	Out of plane CH bending.
750 (w)	-	730 (w)	Out of plane CH bending.
740 (w)	-	-	Out of plane CH bending.
680 (wb)	655 (m)	615 (m)	Out of plane CH deformation.
-	660 (w)	645 (w)	C-S Stretching.
610 (wb)	-	580 (m)	Py. ring deformation.
-	550 (m)	-	COOH Wagging mode.
-	510 (m)	495 (m)	S-S Stretching.
-	-	350 (w)	M-O Stretching.
-	-	320 (m)	M-N Stretching.
-	-	280 (w)	M-S Stretching.

TABLE - 6.07

IR SPECTRAL DATA OF dipy./PDA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	PDA	Ni (dipy.) PDA	Probable assignments
-	-	3420 (mb)	Coordinated H ₂ O mol.
-	1700 (s)	1660 (s)	Asym. C=O Stretching.
1600 (s)	1600 (wm)	1570 (m)	C=N Stretching (Py.)
1585 (m)	1580 (m)	1595 (m)	Aromatic C-C multiple band.
1410 (m)	1455 (m)	1425 (m)	Aromatic C-C multiple band.
-	1480 (m)	1450 (s)	Sym. C=O Stretching.
-	1350 (m)	-	C-O Stretching.
1320 (w)	1310 (m)	1275 (m)	C-N Stretching (Py.)
-	1265 (m)	1200 (m)	C-N Stretching (Py.)
1170 (w)	1170 (m)	1170 (m)	Py. ring.
-	1035 (s)	1045 (w)	C-O Stretching.
-	910 (s)	-	OH deformation.
-	-	840 (mb)	Coordinated H ₂ O mol.
810 (s)	850 (w)	840 (s)	Out of plane CH bending.
750 (w)	745 (m)	765 (m)	Out of plane CH bending.
740 (w)	-	740 (w)	Out of plane CH bending.
-	690 (m)	-	COOH bending.
-	-	680 (mb)	Coordinated H ₂ O mol.
680 (wb)	650 (m)	650 (w)	Out of plane CH deformation.
610 (wb)	600 (m)	605 (m)	Py. ring deformation.
-	520 (s)	-	COOH Wagging mode.
-	-	410 (m)	M-O Stretching.
-	-	380 (m)	M-N Stretching.

TABLE - 6.08

IR SPECTRAL DATA OF dipy./HBAA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	HBAA	Ni (dipy.) HBAA	Probable assignments
-	-	3430 (wb)	Coordinated H ₂ O mol.
-	3450 (sb)	-	OH phenolic Stretching.
-	1640 (s)	1590 (m)	C=N Stretching (Azomethine).
-	1700 (s)	1610 (s)	Asym. C=O Stretching.
1600 (s)	-	1540 (m)	C-N Stretching (Py.)
1585 (m)	1580 (m)	-	Aromatic C-C multiple band.
1410 (m)	-	-	Aromatic C-C multiple band.
-	1400 (m)	1395 (m)	Sym. C=O Stretching.
-	1370 (w)	1350 (wm)	C-O Stretching.
1320 (w)	-	1315 (w)	C-N Stretching (Py.)
-	1365 (m)	-	OH Phenolic bening.
-	1175 (m)	1195 (m)	Phenolic CO Stretching.
1170 (w)	-	1145 (w)	Py. ring.
-	1080 (w)	1080 (w)	Benzene breathing.
-	930 (w)	-	OH deformation.
-	-	820 (wb)	Coordinated H ₂ O mol.
810 (s)	810 (m)	815 (m)	Out of plane CH bending.
750 (w)	755 (s)	750 (s)	Out of plane CH bending.
740 (w)	-	-	Out of plane CH bending.
-	690 (w)	-	COOH bending.
-	-	685 (mb)	Coordinated H ₂ O mol.
680 (wb)	675 (m)	675 (w)	Out of plane CH deformation.
610 (wb)	-	580 (w)	Py. ring deformation.
-	570 (wb)	-	COOH Wagging mode.
-	-	430 (m)	M-O Stretching.
-	-	330 (m)	M-N Stretching.

TABLE - 6.09

IR SPECTRAL DATA OF dipy./HBAT LIGANDS AND THEIR NICKEL COMPLEX

dipy.	HBAT	Ni (dipy.) HBAT	Probable assignments
-	-	3440 (sb)	Coordinated H ₂ O mol.
-	3250 (w)	-	OH phenolic Stretching.
-	2550 (w)	-	S-H Stretching.
-	1635 (s)	1610 (s)	C=N Stretching (Azomethine).
1600 (s)	-	1540 (m)	C-N Stretching (Py.)
1585 (m)	1580 (m)	1580 (m)	Aromatic C-C multiple band.
1410 (m)	1440 (s)	1440 (m)	Aromatic C-C multiple band.
-	1360 (m)	-	CH phenolic bending.
1320 (w)	-	1310 (w)	C-N Stretching (Py.)
-	1175 (w)	1150 (m)	Phenolig CO Stretching.
1170 (w)	-	1175 (m)	Py. ring.
-	960 (w)	960 (m)	Benzene breathing.
-	-	850 (mb)	Coordinated H ₂ O mol.
810 (s)	880 (m)	-	Out of plane CH bending.
750 (w)	750 (s)	755 (m)	Out of plane CH bending.
740 (w)	-	735 (w)	Out of plane CH bending.
680 (wb)	695 (w)	690 (w)	Out of plane CH deformation.
-	-	680 (mb)	Coordinated H ₂ O mol.
-	660 (w)	640 (m)	C-S stretching.
610 (wb)	-	605 (m)	Py. ring deformation.
-	-	470 (m)	M-O Stretching.
-	-	350 (m)	M-N Stretching.
-	-	300 (w)	M-S Stretching.

TABLE - 6.10

IR SPECTRAL DATA OF dipy./DNSA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	DNSA	Ni (dipy.) DNSA	Probable assignments
-	3490 (m)	-	OH phenolic Stretching.
-	1660 (s)	1630 (s)	Asym. C=O Stretching.
1585 (m)	1600 (m)	1585 (m)	Aromatic C-C multiple band.
1600 (s)	-	1550 (m)	C=N Stretching (Py.)
-	1530 (s)	1530 (m)	Aromatic NO ₂ group.
-	1440 (m)	1590 (s)	Sym. C=O Stretching.
1410 (m)	-	1405 (w)	Aromatic C-C multiple band.
-	1380 (m)	1370 (m)	C-O Stretching.
-	1370 (m)	-	OH phenolic bending.
1320 (w)	1330 (m)	1305 (m)	C-N Stretching.
-	1255 (s)	1190 (m)	C-N Stretching.
-	1170 (w)	1115 (m)	Phenolic CO Stretching.
1170 (w)	-	1160 (w)	Py. ring.
-	1100 (w)	1090 (m)	Benzene breathing.
-	1050 (w)	1060 (w)	C-O Stretching.
-	950 (w)	950 (m)	Benzene breathing.
-	930 (m)	-	OH deformation.
810 (s)	850 (mb)	810 (s)	Out of plane CH bending.
750 (w)	740 (s)	750 (s)	Out of plane CH bending.
740 (w)	-	-	Out of plane CH bending.
680 (wb)	720 (m)	710 (m)	Out of plane CH deformation.
-	685 (m)	-	COOH bending.
610 (wb)	-	635 (m)	Py. ring deformation.
-	515 (wb)	-	COOH Wagging mode.
-	-	450 (m)	M-O Stretching.
-	-	330 (w)	M-N Stretching.

TABLE - 6.11

IR SPECTRAL DATA OF dipy./DBSA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	DBSA	Ni (dipy.) DBSA	Probable assignments
-	3240 (m)	-	OH phenolic Stretching.
-	1670 (sb)	1595 (s)	Asym. C=O Stretching.
1600 (s)	-	1550 (s)	C=N Stretching (Py.)
1585 (m)	1590 (m)	1590 (m)	Aromatic C-C multiple band.
1410 (s)	-	1410 (m)	Aromatic C-C multiple band.
-	1420 (m)	1470 (m)	Sym. C=O Stretching.
-	1380 (mb)	-	OH phenolic Stretching.
-	1350 (w)	1370 (w)	C-O Stretching.
1320 (w)	-	1245 (m)	C-N Stretching (Py.)
-	1180 (w)	1110 (w)	Phenolic CO Stretching.
1170 (w)	-	1160 (w)	Py. ring.
-	1100 (w)	1090 (w)	Benzene breathing.
-	910 (w)	-	OH deformation.
810 (s)	800 (mb)	815 (m)	Out of plane CH bending.
750 (w)	780 (w)	750 (w)	Out of plane CH bending.
740 (w)	-	-	Out of plane CH bending.
680 (wb)	710 (m)	700 (m)	Out of plane CH deformation.
-	660 (wb)	-	Out of plane CH deformation.
-	685 (w)	-	COOH bending.
610 (wb)	-	645 (w)	Py. ring deformation.
-	600 (m)	605 (m)	C-Br. Stretching.
-	550 (w)	-	COOH Wagging mode.
-	470 (s)	470 (m)	C-Br. Stretching.
-	-	410 (m)	M-O Stretching.
-	-	380 (m)	M-N Stretching.

TABLE - 6.12

IR SPECTRAL DATA OF dipy./HNA LIGANDS AND THEIR NICKEL COMPLEX

dipy.	HNA	Ni (dipy.) HNA	Probable assignments
-	3450 (w)	-	OH phenolic Stretching.
-	1670 (sb)	1600 (s)	Asym. C=O Stretching.
1600 (s)	-	1620 (s)	C=N Stretching (Py.)
1585 (m)	1585 (m)	1590 (m)	Aromatic C-C multiple band.
-	1480 (mb)	1460 (s)	Sym. C=O Stretching.
1410 (m)	-	1410 (s)	Aromatic C-c multiple band.
-	1380 (m)	1385 (mb)	C-O Stretching.
-	1375 (mb)	-	OH phenolic bending.
1320 (w)	-	1300 (m)	C-N Stretching (Py.)
-	1170 (m)	1215 (m)	Phenolic CO Stretching.
1170 (w)	-	1160 (w)	Py. ring.
-	1100 (w)	1095 (w)	Benzene breathing.
-	1040 (w)	1020 (w)	C-O Stretching.
-	910 (w)	-	OH deformation.
810 (s)	800 (m)	815 (m)	Out of plane CH bending.
750 (s)	760 (w)	760 (w)	Out of plane CH bending.
740 (w)	-	735 (m)	Out of plane CH bending.
-	685 (w)	-	COOH bending.
680 (wb)	660 (m)	660 (w)	Out of plane CH deformation.
610 (wb)	-	640 (m)	Py. ring deformation.
-	550 (m)	-	COOH Wagging mode.
-	-	415 (m)	M-O Stretching.
-	-	325 (m)	M-N Stretching.

TABLE - 6.13

IR SPECTRAL DATA OF dipy./DPDC LIGANDS AND THEIR NICKEL COMPLEX

dipy.	DPDC	Ni (dipy.) DPDC	Probable assignments
-	-	3500 (mb)	Coordinated H ₂ O mol.
-	3400 (w)	3340 (m)	N-H stretching.
-	1660 (s)	1620 (s)	Asym. C=O Stretching.
1600 (s)	-	-	C=N Stretching (Py.)
1585 (m)	1580 (m)	-	Aromatic C-C multiple band.
-	1585 (m)	1575 (m)	N-H bending.
1410 (m)	1450 (m)	-	Aromatic C-C multiple band.
-	1440 (m)	1390 (mb)	Sym. C=O Stretching.
-	1345 (s)	-	C-O Stretching.
1320 (w)	1310 (m)	-	C-N Stretching (Py.)
-	1275 (w)	1240 (m)	C-N Stretching (Py.)
1170 (w)	-	1160 (w)	Py. ring.
-	1075 (m)	1070 (m)	Benzene breathing.
-	920 (s)	-	O-H deformation.
-	-	855 (mb)	Coordinated H ₂ O mol.
810 (s)	810 (m)	810 (sb)	Out of plane CH bending.
750 (w)	785 (m)	760 (s)	Out of plane CH bending.
740 (w)	740 (s)	735 (w)	Out of plane CH bending.
680 (wb)	710 (m)	710 (m)	Out of plane OH deformation.
-	-	690 (mb)	Coordinated H ₂ O mol.
-	650 (m)	660 (w)	Coordinated H ₂ O mol.
-	680 (m)	-	COOH beinding.
610 (wb)	-	640 (mb)	Py. ring deformation.
-	550 (s)	-	COOH Wagging mode.
-	-	410 (m)	M-O Stretching.
-	-	360 (m)	M-N Stretching.

TDAA and DTPA with Cobalt (II) and Copper (II). This is also indication of nickel (II) being linked to TDAA through S atom of $-CH_2S$ group as it does with TDAA and DTAP.

The spectral band due to N-H stretching in free DPDC is found 3400 cm^{-1} . But in the corresponding ternary complex it is found to occurs at 3340 cm^{-1} . Obviously DPDC has coordinated to the nickel atom through N of the N-H group.

In DPDC ligand a moderate band is observed at 1585 cm^{-1} due to the $-N-H$ bending frequency. On complexation with the metal, this frequency too is lowered to confirm our conclusion that nitrogen of $-N-H$ group is involved in coordination.

The HBAA, HBAT, DNSA, DBSA and HNA free ligands exhibit stretching and bending vibration due to $-OH$ (Phenolic) group as bands at 3450 cm^{-1} -3250 cm^{-1} , 3490 cm^{-1} , 3240 cm^{-1} , 3450 cm^{-1} and moderate bands at 1365 cm^{-1} , 1360 cm^{-1} , 1370 cm^{-1} , 1380 cm^{-1} and 1375 cm^{-1} respectively. These bands in free ligand totally disappear on complexation. The nickel metal must, therefore, have linked to the ligands by deprotonation of the phenolic-OH group.

The deprotonation of the S-H group during complexation of free MBA and HBAT having vibration bands at 2590 cm^{-1} and 2550 cm^{-1} is again indicated by disappearance of these frequencies.

The asymmetric and symmetric vibration frequency of CO and OH (acid) group occurring at around 1660 cm^{-1} , 1440 cm^{-1} and 920 cm^{-1} in case of all the relevant ligands are lowered to a significant extent except in the case of Ni

(dipy.) (HBAA) where it goes up a little. This relocation of frequencies indicates that the ligands have coordinated through the carboxylic group.

The stretching frequency $\nu_{C=N}$ of azomethine group in HBAA and HBAT occur as sharp spectral bands at 1640 cm^{-1} and 1635 cm^{-1} respectively. In the corresponding dipy.-nickel complexes, the frequency is lowered by $20\text{--}50\text{ cm}^{-1}$. It is attributed to the coordination of ligand through N of the azomethine group²⁻⁵.

The pyridine group in dipy. and PDA shows $\nu_{C=N}$ at around 1600 cm^{-1} as a moderate spectral band. In the case of nickel (II) complex this frequency is reduced. Further the pyridine ring deformation^{6,7} also hints at nitrogen of pyridine taking part in bond formation with the metal ion.

The free TDPA and DTSA show a weak moderate band at about 590 cm^{-1} and MBA, TDAA and DTPA show it at 570 , 570 and 660 cm^{-1} respectively. This band is attributed to C-S vibration. Again a shift in lower direction in Ni (II) (dipy). ternary complexes to the extent of $30 \pm 10\text{ cm}^{-1}$ is evidence of coordination occurring through S of the C-S group.

The S-S is observed at 500 cm^{-1} and 510 cm^{-1} for DTSA and DTPA respectively. A negative shift in the frequency by 280 cm^{-1} is observed. Ni (dipy.) DTPA. In it is remarkably large of the order of 75 cm^{-1} in the case of Ni (dipy.) DTSA. The S atom has participated in bond formation.

The formation of Ni-O, Ni-N and Ni-S bond in ternary complexes is indicated⁸⁻¹⁰ by new band in the region of $300\text{--}510\text{ cm}^{-1}$, $305\text{--}470\text{ cm}^{-1}$ and $260\text{--}145\text{ cm}^{-1}$.

In the Ni (dipy.) ternary complexes of TDPA, TDAA, PDA, HBAA, HBAT and DPDC a broad band in the region of $3280\text{--}3500\text{ cm}^{-1}$ is observed due to stretching frequency of OH of the coordinated water molecules. The rocking and bending vibration of O-H in the region of $820\text{--}860\text{ cm}^{-1}$ and $680\text{--}690\text{ cm}^{-1}$ respectively are similar to the ones observed earlier. The water molecules are, therefore, firmly coordinated to the nickel (II) ion. Even when a sample of the ternary complex is heated, $120\text{--}180^{\circ}\text{C}$, there is only negligible loss of weight. No further evidence is required to prove that water molecules are coordinated and not trapped in lattice spaces.

6.2.2 Ni phen. Ternary complexes

Tables 6.14 to 6.20 contain the important infra red frequencies of 1:1:1 Ni (phen.) ternary complexes along with tentative assignments. Some of them, as we will see, are vital to establishment of bonding in the structural arrangement of metals and the hetero ligands. Observation of significant alteration in frequencies present in free ligand when they form coordination compounds with nickel (II) give us important clues towards arriving at the structures of ternary complexes.

Spectral bands at 2450 cm^{-1} , 3250 cm^{-1} , 3490 cm^{-1} and 3240 cm^{-1} in HBAA, HBAT, DNSA and DBSA are attributed to stretching and bending frequencies of -OH (phenolic). Complete disappearance of these bands on complexation with nickel (II) - phen-complex is evidence enough to surmise the deprotonation of the -OH group for to form Ni - O - C band. Ni (II), in effect, substitutes the proton.

TABLE - 6.14

IR SPECTRAL DATA OF Phen./MBA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	MBA	Ni (Phen.) MBA	Probable assignments
-	-	-	Coordinated H ₂ O mol.
-	2590 (m)	-	S-H stretching.
-	1690 (s)	1600 (m)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1575 (s)	Aromatic C-C multiple band.
1600 (s)	-	1520 (m)	C=N Stretching (Py.)
1500 (m)	1450 (m)	1455 (w)	Aromatic C-C multiple band.
-	1420 (m)	1490 (m)	Sym. C=O Stretching.
1340 (m)	-	1350 (m)	C-N Stretching (Py.)
1250 (s)	-	1210 (w)	C-N Stretching (Py.)
1165 (w)	-	1145 (m)	Py. ring.
1060 (w)	1060 (w)	1065 (w)	Benzene breathing.
-	1050 (b)	1045 (w)	C-O stretching.
-	930 (m)	-	O-H deformation.
-	-	-	Coordination H ₂ O mol.
800 (s)	910 (m)	840 (m)	Out of plane CH bending.
770 (w)	740 (ms)	770 (w)	Out of plane CH bending.
-	-	-	Coordination H ₂ O mol.
665 (w)	660 (m)	680 (w)	Out of plane OH deformation.
-	680 (m)	-	COOH bending.
630 (w)	-	630 (w)	Py. ring deformation.
-	570 (m)	550 (m)	C-S stretching.
-	520 (w)	-	COOH Wagging mode.
-	-	430 (m)	M-O Stretching.
-	-	390 (w)	M-N Stretching.
-	-	300 (m)	M-S Stretching.

TABLE - 6.15

IR SPECTRAL DATA OF Phen./DTSA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	DTSA	Ni (Phen.) DTSA	Probable assignments
-	1680 (s)	1630 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1590 (m)	Aromatic C-C multiple band.
1600 (s)	-	1560 (m)	C=N Stretching (Py.)
1500 (m)	1480 (m)	1460 (s)	Aromatic C-C multiple band.
-	1415 (s)	1380 (m)	Asym. C=O Stretching.
-	1360 (m)	1350 (w)	C-O Stretching.
1340 (m)	-	1310 (w)	C-N Stretching (Py.)
1250 (m)	-	1210 (m)	C-N Stretching (Py.)
1165 (s)	-	1135 (w)	Py. ring.
1060 (w)	1100 (w)	1050 (m)	Benzene breathing.
-	920 (s)	-	OH deformation.
800 (s)	790 (m)	760 (m)	Out of plane CH bending.
770 (w)	730 (s)	750 (w)	Out of plane CH bending.
-	680 (m)	-	COOH bending.
665 (w)	650 (m)	660 (w)	Out of plane CH deformation.
-	650 (m)	630 (m)	C-S stretching.
630 (w)	-	610 (w)	Py. ring deformation.
-	555 (s)	-	COOH Wagging mode.
-	500 (w)	470 (w)	S-S stretching.
-	-	430 (m)	M-O Stretching.
-	-	350 (w)	M-N Stretching.
-	-	280 (m)	M-S Stretching.

TABLE - 6.16

IR SPECTRAL DATA OF Phen./PDA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	PDA	Ni (Phen.) PDA	Probable assignments
-	-	3500 (sb)	Coordinated H ₂ O mol.
-	1700 (s)	1640 (sb)	Asym. C=O Stretching.
1670 (s)	1580 (m)	1550 (sb)	Aromatic C-C multiple band.
1600 (m)	1600 (s)	1540 (s)	C=N Stretching (Py.)
1500 (s)	1460 (m)	1445 (m)	Aromatic C-C multiple band.
-	1420 (m)	1375 (sb)	Sym. C=O Stretching.
-	1350 (s)	1360 (s)	C-O Stretching (Py.)
1340 (m)	1310 (w)	1290 (s)	C-N Stretching (Py.)
1250 (w)	1265 (s)	1295 (w)	C-N Stretching (Py.)
1165 (m)	1165 (m)	1170 (m)	Py. ring.
1060 (m)	-	1060 (w)	Benzene breathing.
-	1035 (m)	1050 (w)	C-O Stretching.
-	930 (m)	-	OH Stretching.
-	-	810 (wb)	Coordinated H ₂ O mol.
800 (s)	800 (s)	800 (m)	Out of plane CH bending.
770 (w)	740 (w)	760 (m)	Out of plane CH bending.
-	690 (m)	-	COOH bending.
-	-	680 (wb)	Coordinated H ₂ O mol.
665 (m)	650 (m)	670 (m)	Out of plane CH deformation.
630 (w)	600 (m)	600 (w)	Py. ring deformation.
-	520 (s)	-	COOH Wagging mode.
-	-	420 (m)	M-O Stretching.
-	-	340 (m)	M-N Stretching.

TABLE - 6.17

IR SPECTRAL DATA OF Phen./HBAA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	HBAA	Ni (Phen.) HBAA	Probable assignments
-	-	3500 (mb)	Coordinated H ₂ O mol.
-	3450 (w)	-	OH phenolic Stretching.
1670 (s)	-	1660 (w)	Aromatic C-C multiple band.
-	1640 (s)	1580 (s)	C=N Stretching (Azomethine).
-	1620 (s)	15s5	Asym. C=O Stretching.
1600 (m)	-	1550 (s)	C=N Stretching.
1500 (s)	1580 (m)	1500 (s)	Aromatic C-C multiple band.
-	1400 (m)	1360 (s)	Sym. C=O Stretching.
-	1370 (w)	-	C-O Stretching (Py.)
-	1365 (m)	-	OH phenolic bending.
1340 (m)	-	1325 (w)	C-N Stretching (Py.)
1250 (m)	-	1235 (w)	C-N Stretching (Py.)
-	1175 (w)	1130 (m)	Phenolic CO Stretching.
1165 (w)	-	1160 (m)	Py. ring.
1060 (w)	1070 (w)	1070 (w)	Benzene breathing.
-	925 (w)	-	OH deformation.
-	-	850 (mb)	Coordinated H ₂ O mol.
800 (s)	810 (m)	810 (sh)	Out of plane CH bending.
770 (w)	755 (s)	755 (s)	Out of plane CH bending.
-	-	690 (mb)	Coordinated H ₂ O mol.
-	690 (w)	-	COOH bending.
665 (w)	675 (m)	670 (m)	Out of plane CH deformation.
630 (w)	-	625 (w)	Py. ring deformation.
-	570 (wb)	-	COOH Wagging mode.
-	-	430 (m)	M-O Stretching.
-	-	340 (m)	M-N Stretching.

TABLE - 6.18

IR SPECTRAL DATA OF Phen./HBAT LIGANDS AND THEIR NICKEL COMPLEX

Phen.	HBAT	Ni (Phen.) HBAT	Probable assignments
-	-	3445 (mb)	Coordinated H ₂ O mol.
-	3250 (m)	-	OH phenolic stretching.
-	2550 (w)	-	S-H Stretching.
1670 (m)	-	1645 (w)	Aromatic C-C multiple band.
-	1640 (s)	1610 (s)	C=N Stretching (Azomethine).
1600 (s)	-	1550 (m)	C=N Stretching (Py.)
1500 (m)	1580 (m)	1560 (w)	Aromatic C-C multiple band.
-	1440 (s)	1455 (s)	Aromatic C-C multiple band.
-	1360 (m)	-	OH phenolic stretching.
1340 (m)	-	1300 (m)	C-N Stretching (Py.)
1250 (m)	-	1220 (s)	C-N Stretching (Py.)
-	1170 (w)	1140 (w)	Phenolic CO Stretching.
1165 (m)	-	1160 (m)	Py. ring.
1160 (w)	960 (m)	1040 (m)	Benzene breathing.
800 (s)	850 (w)	830 (w)	Out of plane CH bending.
-	-	810 (wb)	Coordinated H ₂ O mol.
770 (w)	740 (s)	740 (m)	Out of plane CH bending.
-	-	690 (mb)	Coordinated H ₂ O mol.
665 (w)	690 (m)	670 (w)	Out of plane CH deformation.
-	660 (w)	640 (m)	C-S Stretching.
630 (w)	-	625 (w)	Py. ring deformation.
-	-	410 (m)	M-O Stretching.
-	-	370 (m)	M-N Stretching.
-	-	270 (m)	M-S Stretching.

TABLE - 6.19

IR SPECTRAL DATA OF Phen./DNSA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	DNSA	Ni (Phen.) DNSA	Probable assignments
-	-	-	Coordinated H ₂ O mol.
-	3490 (m)	-	OH phenolic stretching.
-	1680 (s)	1620 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	-	Aromatic C-C multiple band.
1600 (s)	-	1540 (s)	C=N Stretching (Py.)
1500 (m)	-	1510 (m)	Aromatic C-C multiple band.
-	1470 (s)	1460 (m)	Sym. C=O Stretching.
-	1380 (m)	1355 (s)	C-O Stretching (Py.)
-	1370 (m)	-	OH phenolic bending.
1340 (m)	1330 (m)	1300 (s)	C-N Stretching.
1250 (m)	1255 (b)	1200 (m)	C-N Stretching.
-	1175 (w)	1125 (m)	Phenolic CO Stretching.
1165 (m)	-	1160 (m)	Py. ring.
-	1090 (w)	-	Benzene breathing.
-	1050 (w)	-	C-O Stretching.
-	960 (w)	960 (w)	Benzene breathing.
-	930 (m)	-	OH deformation.
800 (s)	-	-	Coordinated H ₂ O mol.
770 (w)	840 (m)	800 (m)	Out of plane CH bending.
665 (w)	730 (m)	760 (w)	Out of plane CH bending.
630 (w)	715 (mb)	700 (mb)	Out of plane CH deformation.
-	680 (s)	670 (m)	Py. ring deformation.
-	-	-	Coordinated H ₂ O mol.
-	515 (wb)	-	COOH Wagging mode.
-	-	430 (m)	M-O Stretching.
-	-	320 (m)	M-N Stretching.

TABLE - 6.20

IR SPECTRAL DATA OF Phen./DBSA LIGANDS AND THEIR NICKEL COMPLEX

Phen.	DBSA	Ni (Phen.) DBSA	Probable assignments
-	-	3300 (wb)	Coordinated H ₂ O mol.
-	3240 (w)	-	OH phenolic stretching.
-	1670 (sb)	1600 (s)	Asym. C=O Stretching.
1670 (m)	1600 (m)	1610 (m)	Aromatic C-C multiple band.
1600 (s)	-	1550 (s)	C-N Stretching (Py.)
1500 (m)	-	1505 (m)	Aromatic C-C multiple band.
-	1420 (mb)	1395 (m)	Sym. C=O Stretching.
-	1380 (m)	-	OH phenolic bending.
-	1350 (w)	1310 (m)	C-O Stretching (Py.)
1340 (m)	-	1265 (w)	C-N Stretching.
1250 (m)	-	-	C-N Stretching.
-	1170 (w)	1160 (m)	Phenolic CO Stretching.
1165 (mb)	-	1150 (w)	Py. ring.
1060 (w)	1100 (w)	1060 (m)	Benzene breathing.
-	815 (w)	-	OH deformation.
-	-	840 (m)	Coordinated H ₂ O mol.
800 (s)	860 (mb)	-	Out of plane CH bending.
770 (w)	770 (w)	800 (m)	Out of plane CH bending.
665 (w)	720 (w)	730 (w)	Out of plane CH deformation.
-	-	685 (wb)	Coordinated H ₂ O mol.
-	660 (m)	660 (m)	Coordinated H ₂ O mol.
-	690 (m)	-	COOH bending.
630 (w)	-	625 (w)	Py. ring deformation.
-	600 (m)	600 (m)	C-Br Stretching.
-	550 (w)	-	COOH Wagging mode.
-	470 (s)	475 (w)	C-Br Stretching.
-	-	395 (m)	M-O Stretching.
-	-	340 (m)	M-N Stretching.

Free MBA and HBAT show weak spectral bands at 2590 cm^{-1} and 2550 cm^{-1} respectively. These bands are attributed to S-N stretching vibrations. However, as in the case of phenolic - OH, the bands disappear on complexation in the case of these ligands too. Hence the proton of the - SH group must have been replaced by Ni (II) on to form a similar Ni - S - C band.

The CO group of carboxylic ligands exhibit asymmetric and symmetric stretching vibrations as sharp bands in the region of $1620\text{-}1700\text{ cm}^{-1}$, $1400\text{-}1475\text{ cm}^{-1}$. The OH group of the carboxylic ligands manifest their deformation vibration as bands around $920 \pm 10\text{ cm}^{-1}$. When, however, the carboxylic ligands form a complex, the CO frequencies shift towards the lower side and OH deformation frequencies disappear altogether. It is a clear suggestion that nickel is coordinating with such ligands through carboxylic group.

Sharp infra red bands around 1640 cm^{-1} and 1635 cm^{-1} are seen due to C=N stretching vibration of azomethic group in HBAA and HBAT. There is a shift of about $25\text{-}55\text{ cm}^{-1}$ in the corresponding nickel - phen. Complexes²⁻⁵. thus, N of the azomethrine group is taking part in coordination phenomenon in the case of these two ligands.

There is a remarkable shift of around 40 cm^{-1} in the stretching frequencies of C=N of pyridine group present in free phen. and PDA ligands. In the free ligands it is of the order of 1600 cm^{-1} . It suggests pyridine N is taking part in coordination. In fact, pyridine ring deformation vibration also shifts to the lower region to confirm that N of the pyridine ring has actually linked by coordination to the metal.

The C-S stretching utilization for MBA and DTSA occur at 570 cm^{-1} and 650 cm^{-1} and at 660 cm^{-1} for HBAT. On complexation with Ni (phen.) these frequencies are lowered by $5\text{-}30\text{ cm}^{-1}$ leaving no doubt that S atom of these thioacids has directly coordinated with Ni (II) ion.

Free DTPA has a band at 500 cm^{-1} attributed to vs-s stretching frequency. This shifts to a lower side in Ni (phen.) DTPA complex. Here again a Ni-S bond must have formed.

In the formation of ternary complexes with nickel, new bands appear in the region of $395\text{-}480\text{ cm}^{-1}$ and $320\text{-}405\text{ cm}^{-1}$. It is clear indication that ligands are coordinating through O and N atoms to form Ni-O and Ni-N bonds.

When MBA, DBSA, PDA, HBAA, HBAT and DNSA form ternary complexes with Ni (phen.), a broad band in the region of $3410\text{-}3550\text{ cm}^{-1}$ is seen. It is attributed the stretching vibration of OH of the coordinated water molecule. The appearance of rocking and bending vibration of OH in the region of $810\text{-}850\text{ cm}^{-1}$ supports the contention that water molecules are actually coordinated to the central metal ion as proposed by Nakamoto¹¹.

6.3. Magnetic Studies

The magnetic studies of the Ni (II) ternary complexes were carried out as those already reported for copper (II) and nickel (II) metals in the previous two chapters. Table 6.21 contains the results of these studies.

The data reveals that for the four coordinate shape, tetrahedral configuration has two unpaired electrons and square planar configuration has

TABLE 6.21

MAGNETIC MEASUREMENT DATA OF Ni (II) COMPLEXES

Compound	Molar susceptibility 'K _M ' = K' x M X 10 ⁻⁶	Diamagnetic correction (Dia) X 10 ⁻⁶	Corrected Molar susceptibility K _M (Dia) X 10 ⁻⁶	Curie's value 'C' = K _M (Dia) ^{1/2} (T=300±2°K) X 10 ⁻⁶	Magnetic susceptibility 'μ _{eff} ' = 2.84 √C(BM)	Number of unpaired e ⁻	Hybridization
Ni (dipy) TDPA. H ₂ O	4005.4487	-206	4211.4487	1255011.70	3.18	2	Sp ³ d ²
Ni (dipy) MBA	226.0506	-184	410.0506	122195.07	0.99	Zero	dsp ²
Ni (dipy) TDAA. H ₂ O	3465.6061	-182	3647.6061	1094281.80	2.97	2	Sp ³ d ²
Ni (dipy) DTSA	3500.1890	-261	3761.1890	1135879.07	3.02	2	Sp ³ d ²
Ni (dipy) DTPA. H ₂ O	3517.5301	-210	3727.5300	1118259.00	3.00	2	Sp ³ d ²
Ni (dipy) DPA. H ₂ O	3159.6856	-186	3345.6856	1003705.60	2.84	2	Sp ³ d ²
Ni (dipy) HBAA. H ₂ O	4098.9009	-247	4345.9009	1295078.40	3.23	2	Sp ³ d ²
Ni (dipy) HBAT. H ₂ O	4109.6347	-247	4356.6347	1298277.10	3.23	2	Sp ³ d ²
Ni (dipy) DNSA	316.22888	-182	498.22888	149468.66	1.09	Zero	dsp ²
Ni (dipy) DBSA	3581.4397	-229	3810.4397	1143131.90	3.03	2	Sp ³ d ²
Ni (dipy) HNA	283.00494	-205	488.00494	146401.48	1.08	Zero	dsp ²
Ni (dipy) DPDC. H ₂ O	3721.9398	-250	397.9398	1183638.00	3.09	2	Sp ³ d ²
Ni (phen) MBA	253.21787	-221	474.21787	141316.92	1.06	Zero	dsp ²
Ni (phen) DTSA	3239.0006	-298	3537.0006	1054026.10	2.91	2	Sp ³ d ²
Ni (phen) PDA. H ₂ O	3540.7836	-225	3765.7836	1129735.00	3.02	2	Sp ³ d ²
Ni (phen) HBAA. H ₂ O	3176.6798	-285	3461.6798	1045427.20	2.90	2	Sp ³ d ²
Ni (phen) HBAT. H ₂ O	3362.9797	-287	3649.9797	1102293.80	2.98	2	Sp ³ d ²
Ni (phen) DNSA	3792.4520	-233	4025.4520	1215384.50	3.13	2	Sp ³
Ni (phen) DBSA. H ₂ O	3692.4849	-287	3979.4849	1193845.40	3.10	2	Sp ³ d ²

no unpaired electron. The octahedral complexes of nickel (II) also have two unpaired electrons.

In the present investigations μ_{eff} of 2.84 – 3.23 BM is observed in all ternary complexes of nickel (II) except Ni (dipy.) MBA, Ni (dipy.) DNSA, Ni (dipy.) HNA and Ni (phen.) MBA. Other investigators¹²⁻¹⁴ have found μ_{eff} of the range of 2.9-3.3 B.M. for octahedral complexes with two unpaired electrons. Thus, the expectation was of spin free octahedral complexes with sp^3d^2 hybridization. But, there are two exceptions i.e. Ni (dipy.) DBSA and Ni (phen.) DNSA ternary complexes where tetrahedral geometry due to sp^3 hybridization is postulated on account of absence of coordinated water molecules. This has been borne out by IR studies.

The low μ_{eff} of 0.99, 1.09, 1.00 and 1.06 BM for Ni (dipy.) MBA, Ni (dipy.) DNSA, Ni (dipy.) HNA and Ni (phen.) MBA mixed complexes respectively is ascribed¹⁵ to thermal population of the triplet which lies close the singlet ground state. It also could be interpreted to mean a tendency towards polymersisation in the solid state. It has been postulated here that there is weak axial coordination due to which the shape is effectively square planer with spin paired configuration with no unpaired electron.

On the basis of studies reported above, the bonding structures of the nickel (II) mixed complexes are depicted in fig. 6.1 to 6.5.

BONDING STRUCTURES OF BIPYRIDINE NICKEL (II) COMPLEXES

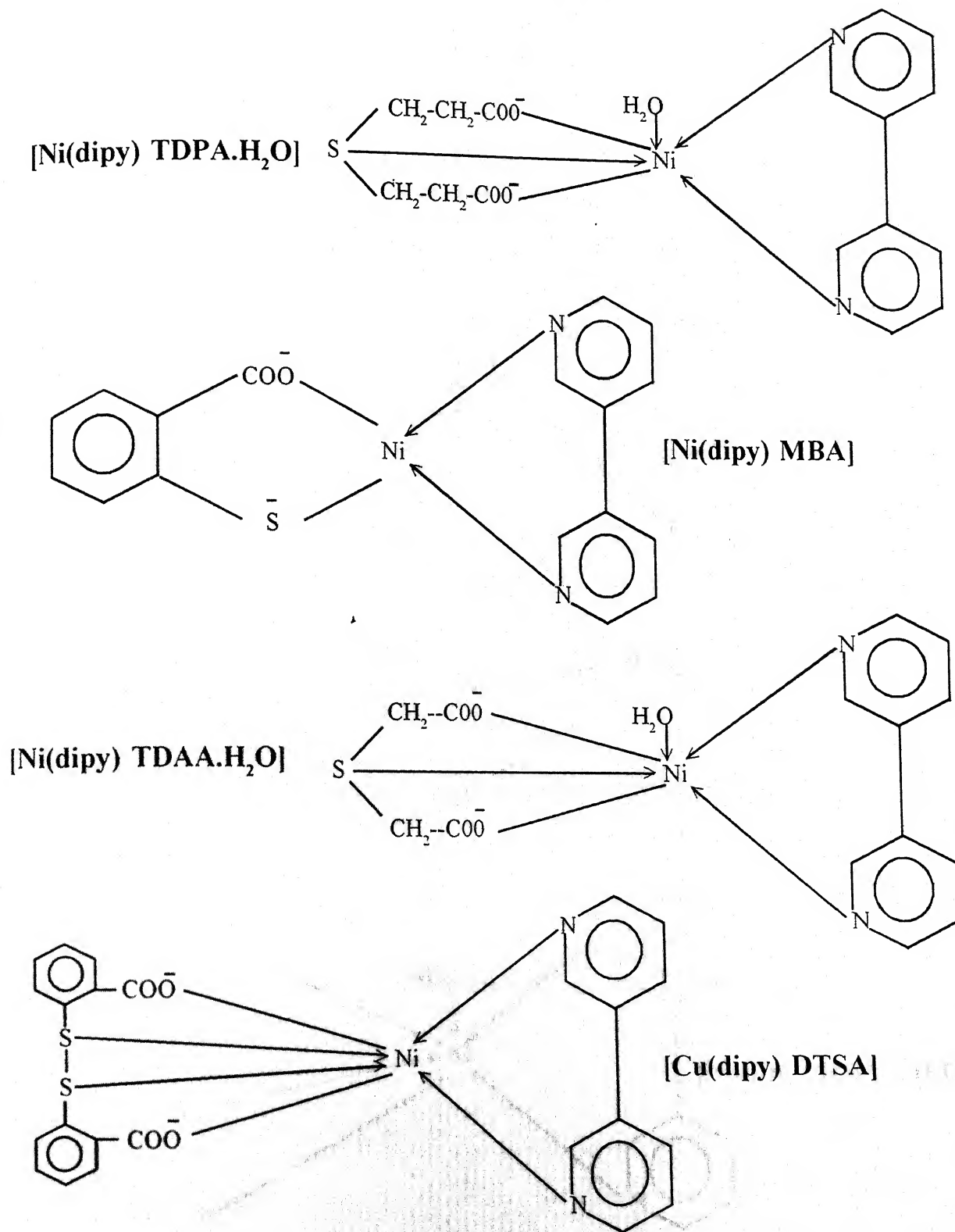


FIGURE 6.1

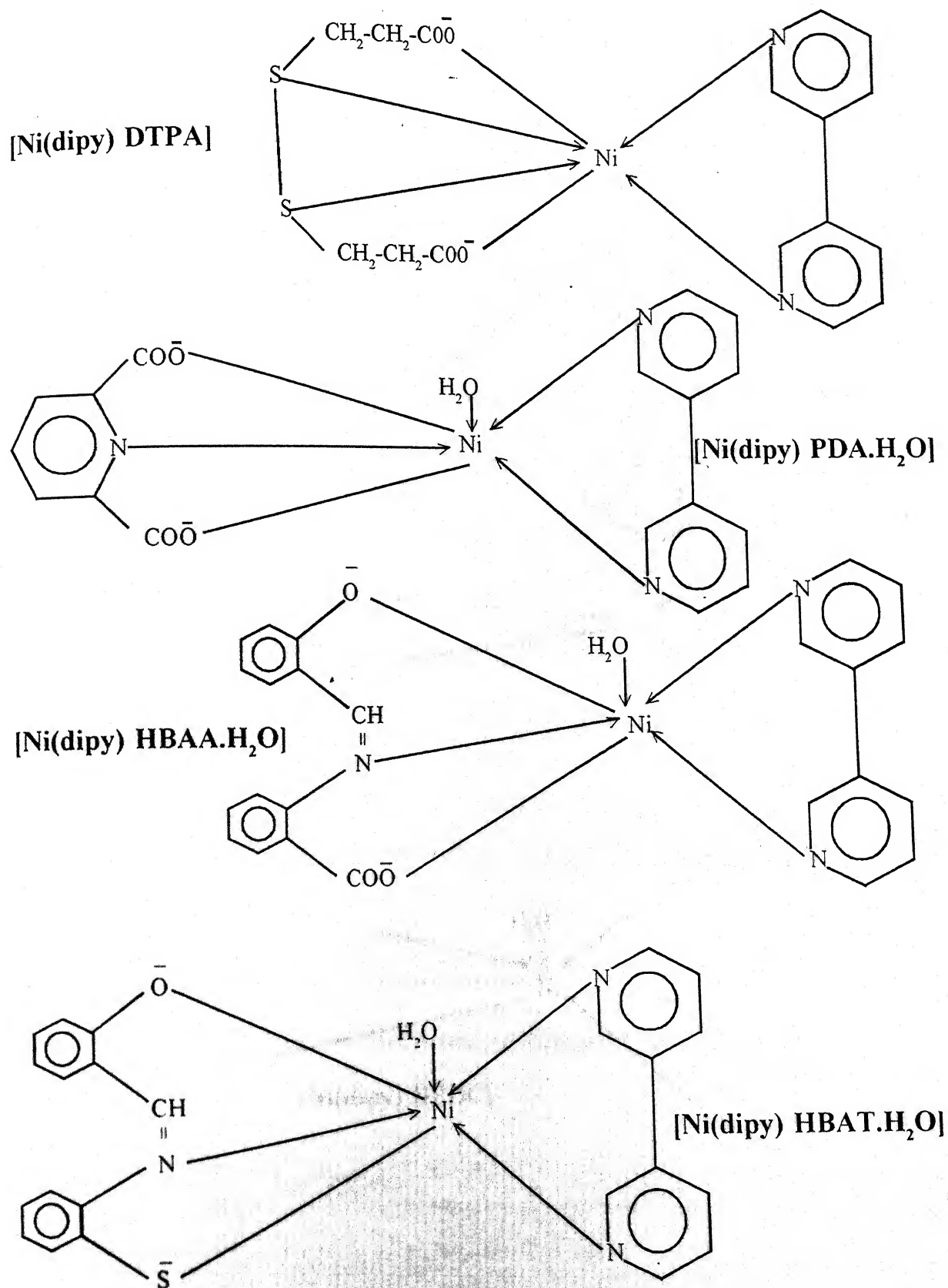


FIGURE 6.2

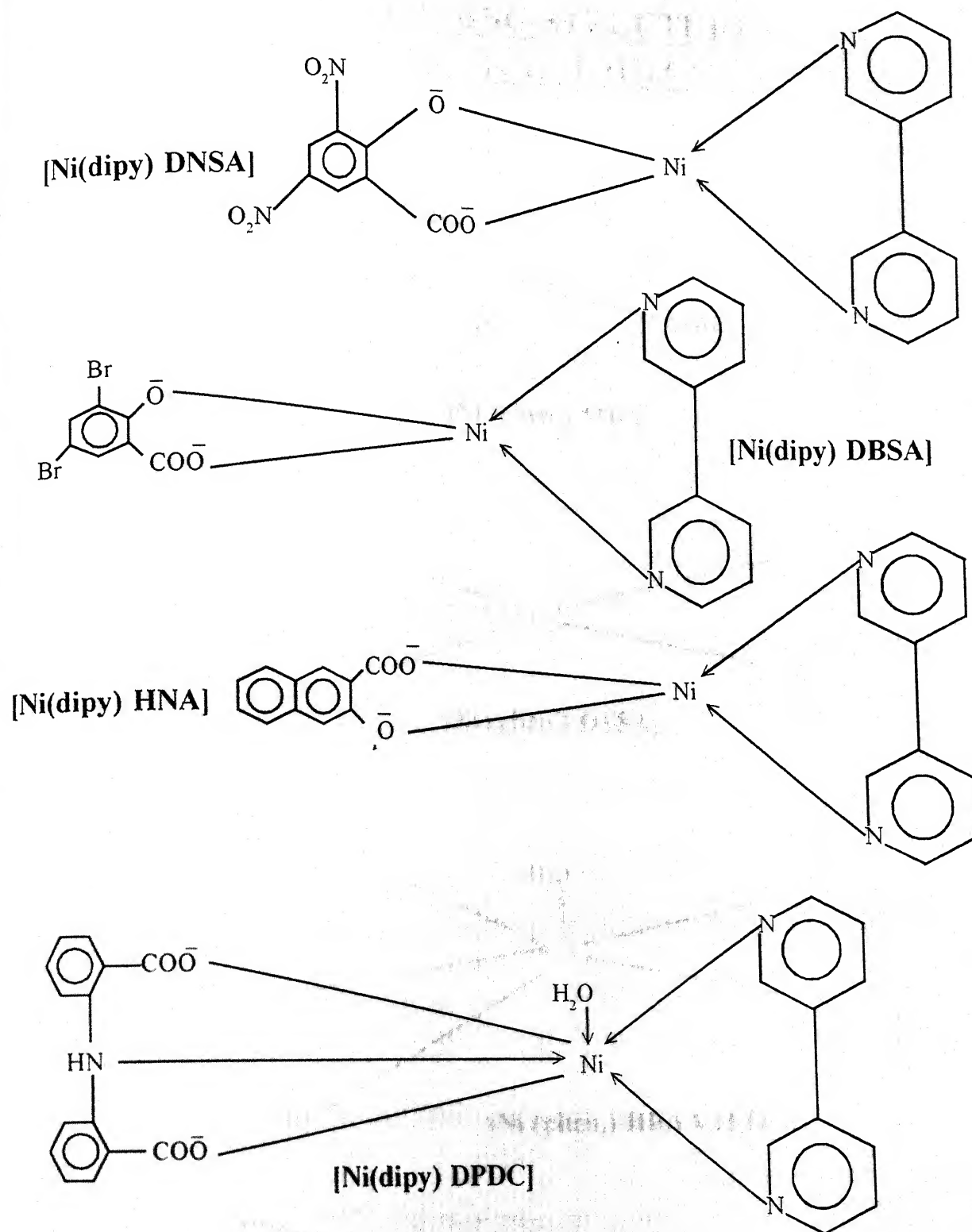


FIGURE 6.3

PROPOSED BONDING STRUCTURES OF PHENANTHROLINE NICKEL (II) COMPLEXES

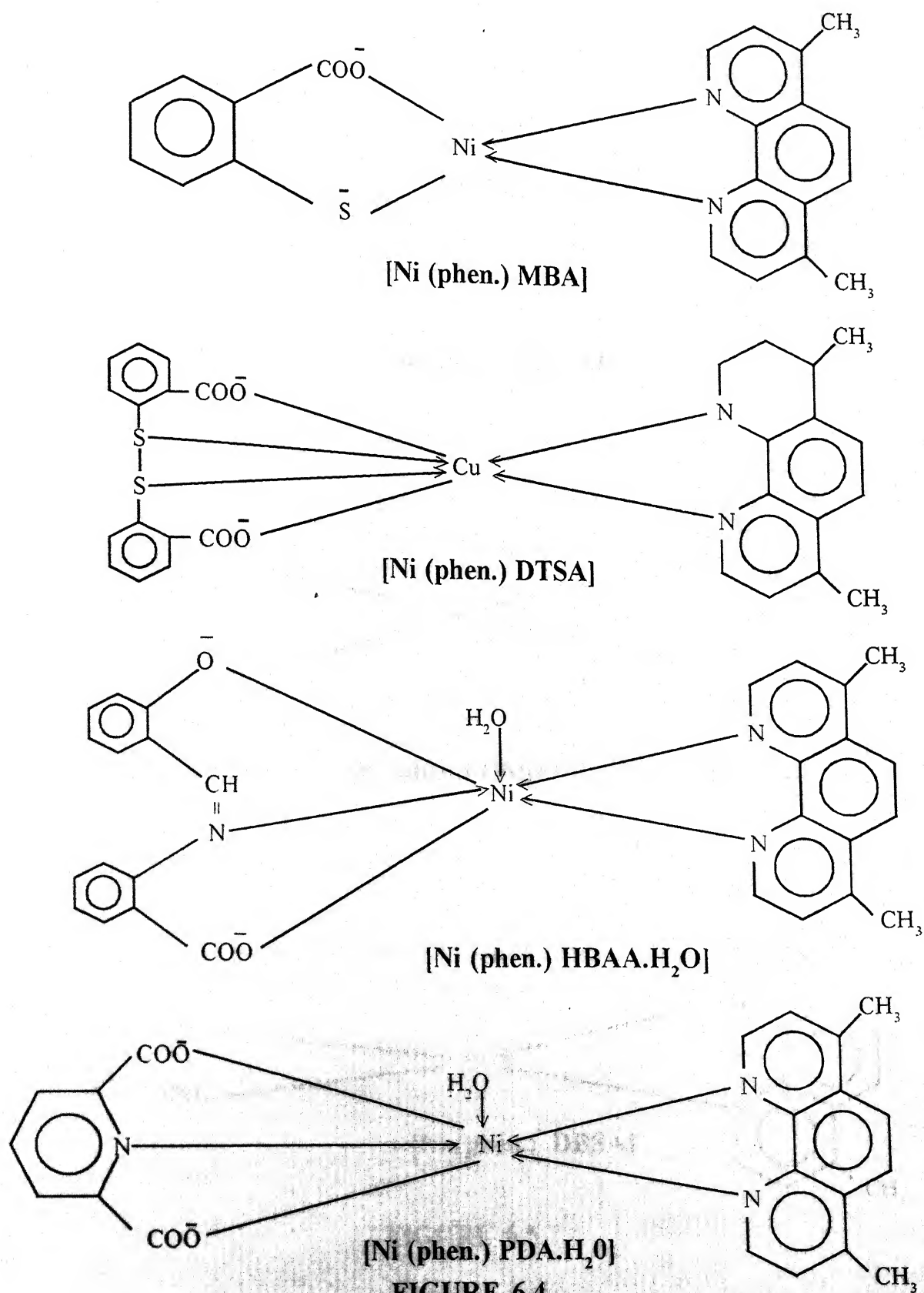


FIGURE 6.4

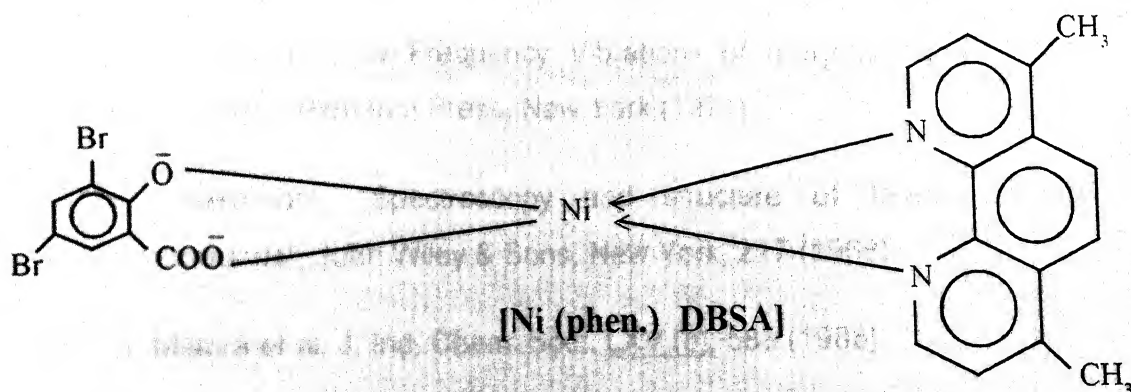
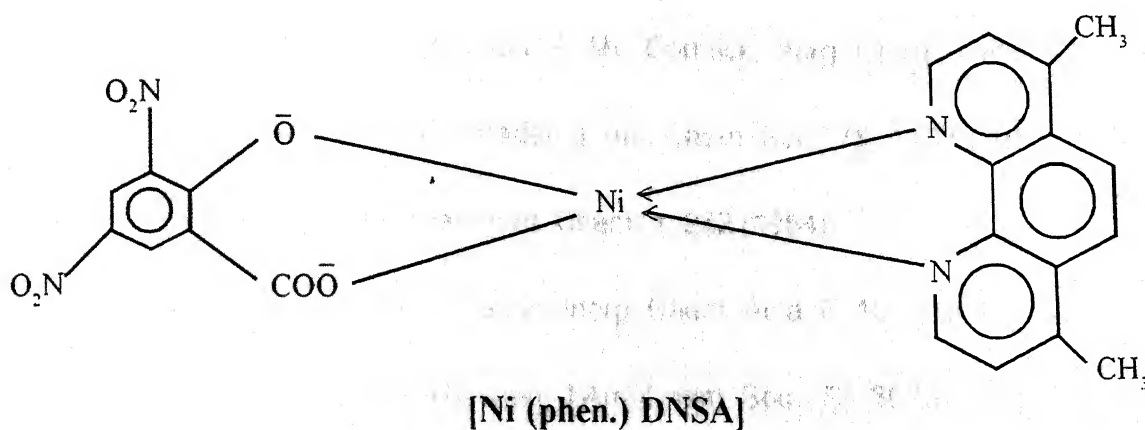
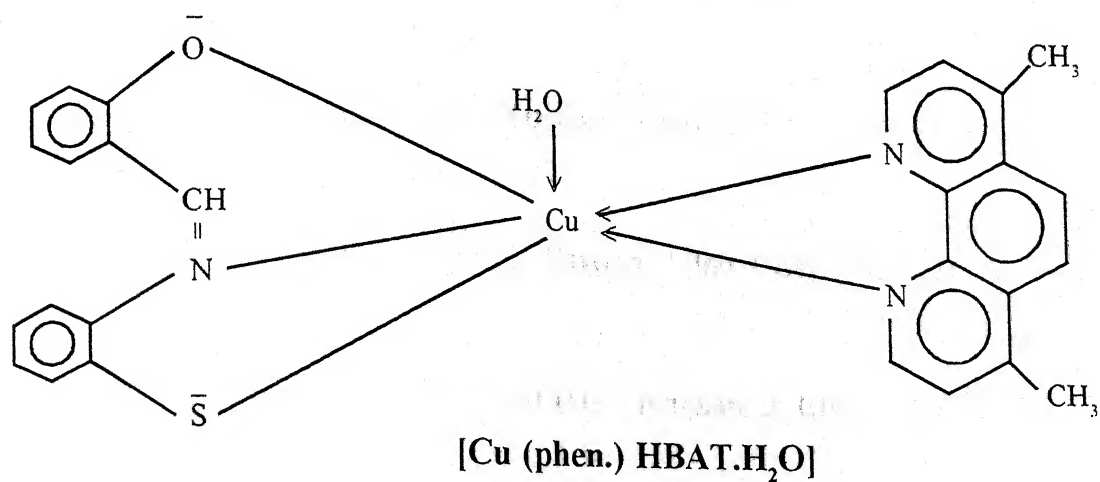


FIGURE 6.5

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CHAPTER - 7

CHAPTER - VII

MICROBIAL STUDIES

As already stated, the antifungal and antibacterial properties of the synthesized ligands and all the metal chelates under investigation were studied as per procedure outlined on selected bacteria and fungi. The details of results obtained are described in the following lines.

7.1 Results and Discussion

The data obtained following microbial investigations have been detailed in tables 7.01 to 7.04.

7.1.1 Microbial activity

A look at the results obtained at once leads us to the conclusion that, in general, the microbial activity of metal chelates synthesized is greater than the metals or the ligands alone. It is also notable that with increase in ligand concentration in a complex, inhibition of growth rate of fungi and bacteria increases.

All the metal – dipyrindine ternary complexes with the exception of Ni (dipy.) TDPA and Cu (dipy.) TDAA and even Co (dipy.) DBSA show negligible activity against *Aspergillus flavus* and *A. Niger*. The inactivity of Ni (dipy.) DTSA towards test fungi and Co (dipy.) DTSA towards test bacteria may be attributed to the bioactive effect of metal ion, ligand present in the complex and trace elements present in the fungi and bacteria species.

TABLE - 7.01

**ANTIFUNGAL AND ANTIBACTERIAL ACTIVITY OF THE LIGANDS AND SOLVENTS
AT 500 ppm AND 32°C TEMPERATURE**

Ligand	Bacterial growth after 2 days		Fungal growth after 7 days		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
dipy.	-	-	-	-	-
phen.	++	+	-	-	-
TDPA	+	+	++	+	++
MBA	++++	++	+	+++	+
TDAA	+	+	++	++	+
DTSA	-	-	-	-	-
DTPA	-	-	-	-	-
PDA	-	-	-	-	-
HBAA	+++	++	++	++++	+++
HBAT	-	-	-	-	-
DNSA	-	-	-	-	-
DBSA	-	-	-	-	-
HNA	-	-	+	+	+
IMDA	++	+	-	-	-
DPDC	-	-	-	-	-
DMF	++++	++++	++++	++++	++++
DMSO	++++	++++	++++	++++	++++
G1	++++	++++	++++	++++	++++

++++ = Very high growth of Bacteria of fungi.

+++ = High growth of bacteria of fungi.

++ = Moderate growth of bacteria of fungi.

+ = Poor growth of bacteria of fungi.

- = No growth of bacteria or fungi.

TABLE - 7.02

**ANTIFUNGAL AND ANTIBACTERIAL ACTIVITY OF Cu-CHELATES AT 500 ppm
AND 32°C TEMPERATURE**

Cu-chelate	Bacterial growth after 2 days		Fungal growth after 7 days		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Cu (dipy.) TDPA	-	-	+	+	+
Cu (dipy.) MBA	+	+	+	+	+
Cu (dipy.) TDAA	-	-	-	-	-
Cu (dipy.) DTSA	-	-	-	-	-
Cu (dipy.) DTPA	-	-	-	-	-
Cu (dipy.) PDA	-	-	-	-	-
Cu (dipy.) HBAA	-	-	-	-	-
Cu (dipy.) HBAT	-	-	+	-	+
Cu (dipy.) DNSA	+	+++	+	+++	+
Cu (dipy.) HNA	-	-	-	-	-
Cu (dipy.) IMDA	-	-	-	-	-
Cu (dipy.) DPDC	-	-	-	-	-
Cu (phen.) MBA	+++	+	+	+	+
Cu (phen.) DTSA	-	-	-	-	-
Cu (phen.) DTPA	-	-	-	-	-
Cu (phen.) PDA	-	-	-	-	-
Cu (phen.) HBAA	-	-	+	+	+
Cu (phen.) HBAT	++	+	++	++	+
Cu (phen.) DNSA	+++	+	+	+	+
Cu (phen.) DBSA	+	+	+	-	-

+++ = High growth of bacteria of fungi.

++ = Moderate growth of bacteria of fungi.

+ = Poor growth of bacteria of fungi.

- = No growth of bacteria or fungi.

TABLE - 7.03

**ANTIFUNGAL AND ANTIBACTERIAL ACTIVITY OF Co-CHELATES AT 500 ppm
AND 32°C TEMPERATURE**

Co-chelate	Bacterial growth after 2 days		Fungal growth after 7 days		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Co (dipy.) TDPA	-	-	+	-	+
Co (dipy.) MBA	-	-	-	-	+
Co (dipy.) TDAA	-	-	+	-	-
Co (dipy.) DTSA	+	++	+	-	-
Co (dipy.) DTPA	-	-	-	+++	-
Co (dipy.) PDA	-	-	+	+	+
Co (dipy.) HBAA	-	-	-	-	-
Co (dipy.) HBAT	+	+	-	+	-
Co (dipy.) DNSA	-	-	-	-	+
Co (dipy.) DBSA	++	+	+	+++	-
Co (dipy.) HNA	-	-	-	+	-
Co (phen.) MBA	-	-	-	-	-
Co (phen.) DTSA	-	-	+	-	-
Co (phen.) PDA	-	-	+++	-	+
Co (phen.) HBAA	+	+	-	-	-
Co (phen.) HBAT	-	-	-	-	-
Co (phen.) DNSA	-	-	-	++	-
Co (phen.) DBSA	+	+	-	+	+

+++ = High growth of bacteria of fungi.

++ = Moderate growth of bacteria of fungi.

+ = Poor growth of bacteria of fungi.

- = No growth of bacteria or fungi.

TABLE – 7.04

**ANTIFUNGAL AND ANTIBACTERIAL ACTIVITY OF Ni-CHELATES AT 500 ppm
AND 32°C TEMPERATURE**

Ni-chelate	Bacterial growth after 2 days		Fungal growth after 7 days		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Ni (dipy.) TDPA	-	-	+	-	-
Ni (dipy.) MBA	-	-	-	-	-
Ni (dipy.) TDAA	-	-	-	++	-
Ni (dipy.) DTSA	-	-	+	+	+
Ni (dipy.) DTPA	-	-	-	-	-
Ni (dipy.) PDA	-	-	+	-	+
Ni (dipy.) HBAA	-	-	+	-	-
Ni (dipy.) HBAT	-	-	-	-	-
Ni (dipy.) DNSA	-	-	-	-	-
Ni (dipy.) DBSA	-	-	+	-	-
Ni (dipy.) HNA	-	-	-	+	+
Ni (dipy.) DPDC	++	-	-	-	-
Ni (phen.) MBA	-	-	-	-	-
Ni (phen.) DTSA	-	-	-	+	-
Ni (phen.) PDA	-	-	-	-	-
Ni (phen.) HBAA	-	-	-	-	-
Ni (phen.) HBAT	-	-	-	-	-
Ni (phen.) DNSA	-	-	-	-	-
Ni (phen.) DBSA	-	-	-	+	-

++ = Moderate growth of bacteria or fungi.

+ = Poor growth of bacteria or fungi.

- = No growth of bacteria or fungi.

In the case of Cu (II) – (phen.) complexes with MBA, HBAT and DTSA, the negligible activities observed against *Staphylo cococus aureus* and *Escherichia coli* may be attributed to poor anti-bacterial activities of (phen.). This poor activity is found only in Cu (II) complexes due to the bioactive action of the metal ion. In Cu (dipy.) and Cu (phen.) complexes with DNSA, the NO_2^- present in the latter is responsible for almost total inactivity of these mixed complexes on test bacteria and fungi.

If the geometry and charge distribution around the periphery of pores of the fungal and bacterial cell wall is not compatible with the geometry of the attacking species, the penetration of the toxic agent is almost impossible and hence such species are biologically inactive and toxic effect fails to be effective. This is why some ternary complexes have less anti-microbial activity than corresponding ligands alone.

7.1.2 MIC Values of metal chelates

The minimum inhibitory concentration (MIC) values of the ligands and then mixed complexes have been listed in tables 7.05 to 7.10.

A comparative microbial activity picture emerges from a careful perusal of data in these tables.

Obviously, the mixed ligand complexes of Ni (phen.) are the most effective agents against the test fungi and the test bacteria.

In case of dipy mixed ligand complexes the microbial activity is dependent upon the nature of the other ligand or the combined effect of the other ligand and the metal present. No generalization is possible in such cases. A lot of additional data might be required in order to fully understand the causes of such a behaviour.

TABLE – 7.05

MIC-VALUE OF LIGANDS AND METAL ACETATES IN ppm

Compound	Bacteria		Fungi		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
dipy	400	300	500	400	500
phen	> 500	> 500	400	500	300
DTSA	400	300	400	500	400
DTPA	500	500	300	400	300
PDA	400	300	500	400	500
HBAT	300	500	400	400	300
DNSA	500	400	500	500	400
DBSA	400	500	500	300	400
HNA	300	400	> 500	> 500	> 500
IMDA	> 500	> 500	400	400	300
DPDC	300	500	500	400	500
Cu-acetate	400	400	500	400	500
Co-acetate	500	400	300	500	400
Ni-acetate	400	300	500	400	300

TABLE - 7.06
MIC-VALUE OF Cu-CHELATES IN ppm

Cu-chelates	Bacteria		Fungi		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Cu (dipy.) TDPA	200	200	> 500	> 500	> 500
Cu (dipy.) TDAA	300	100	200	300	100
Cu (dipy.) DTSA	< 100	< 100	100	400	200
Cu (dipy.) DTPA	< 100	< 100	< 100	100	< 100
Cu (dipy.) PDA	< 300	200	400	400	200
Cu (dipy.) HBAA	200	100	400	100	100
Cu (dipy.) HBAT	100	100	> 500	300	> 500
Cu (dipy.) HNA	< 100	< 100	200	100	< 100
Cu (dipy.) IMDA	< 100	< 100	400	200	100
Cu (dipy.) DTDC	< 100	< 100	400	300	100
Cu (phen.) DTSA	100	200	300	100	200
Cu (phen.) DTPA	< 100	100	100	200	200
Cu (phen.) PDA	< 100	< 100	< 100	< 100	< 100
Cu (phen.) HBAA	100	200	> 500	> 500	> 500
Cu (phen.) DBSA	> 500	> 500	> 500	300	200

TABLE – 7.07

MIC-VALUE OF Co-CHELATES IN ppm

Co-chelates	Bacteria		Fungi		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Co (dipy.) TDPA	100	300	> 500	200	> 500
Co (dipy.) MBA	200	100	100	< 100	> 500
Co (dipy.) TDAA	300	< 100	> 500	200	200
Co (dipy.) DTSA	> 500	> 500	> 500	< 100	300
Co (dipy.) DTPA	< 100	100	< 100	> 500	200
Co (dipy.) PDA	< 100	< 100	> 500	> 500	> 500
Co (dipy.) HBAA	400	200	300	300	400
Co (dipy.) HBAT	> 500	> 500	100	> 500	< 100
Co (dipy.) DNSA	< 100	100	300	< 100	> 500
Co (dipy.) DBSA	> 500	> 500	> 500	> 500	300
Co (dipy.) HNA	200	< 100	100	> 500	400
Co (phen.) MBA	400	400	200	300	400
Co (phen.) DTSA	< 100	300	> 500	< 100	100
Co (phen.) PDA	300	200	> 500	500	> 500
Co (phen.) HBAA	> 500	> 500	300	100	200
Co (phen.) HBAT	< 100	200	< 100	200	400
Co (phen.) DNSA	< 100	100	100	> 500	200
Co (phen.) DBSA	> 500	> 500	200	> 500	> 500

TABLE - 7.08

MIC-VALUE OF Ni-CHELATES IN ppm

Ni-chelates	Bacteria		Fungi		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
Ni (dipy.) TDPA	100	200	> 500	200	300
Ni (dipy.) MBA	400	400	400	400	300
Ni (dipy.) TDAA	200	300	100	> 500	< 100
Ni (dipy.) DTSA	300	100	> 500	> 500	> 500
Ni (dipy.) DTPA	100	200	300	< 100	300
Ni (dipy.) PDA	100	300	> 500	400	> 500
Ni (dipy.) HBAA	< 100	400	> 500	400	300
Ni (dipy.) HBAT	300	200	< 100	< 100	300
Ni (dipy.) DNSA	100	300	200	400	< 100
Ni (dipy.) DBSA	200	< 100	> 500	< 100	300
Ni (dipy.) HNA	300	200	100	> 500	> 500
Ni (dipy.) DPDC	> 500	< 100	< 100	300	300
Ni (phen.) MBA	300	100	100	300	100
Ni (phen.) DTSA	200	100	100	> 500	< 100
Ni (phen.) PDA	400	200	200	< 100	200
Ni (phen.) HBAA	200	< 100	< 100	100	100
Ni (phen.) HBAT	200	100	200	300	300
Ni (phen.) DNSA	300	400	< 100	300	100
Ni (phen.) DBSA	400	100	200	> 500	300

TABLE – 7.09

ORDER OF MIC-VALUE OF dipy-COMPLEXES IN TERMS OF METAL IONS

Ligand	Bacteria		Fungi		
	S. aureus	E. coli	A. flavus	A. fumigatus	A. niger
TDPA	Cu>Ni=Co	Co>Ni=Cu	Cu=Ni=Co	Cu>Ni=Co	Cu=Ni>Co
MBA	Cu>Ni=Co	Cu>Ni>Co	Cu>Ni>Co	Cu>Ni>Co	Cu=Co>Ni
TDAA	Cu=Co>Ni	Ni>Cu>Co	Co>Cu>Ni	Ni>Cu>Co	Co>Cu>Ni
DTSA	Co>Ni>Cu	Co>Ni=Cu	Co=Ni>Cu	Ni>Cu>Co	Ni>Co>Cu
DTPA	Cu=Ni>Co	Ni>Co=Cu	Ni>Co=Cu	Co>Cu>Ni	Ni>Co>Cu
PDA	Cu>Ni>Co	Ni>Cu>Co	Co=Ni>Ni	Co>Ni=Cu	Co=Ni>Cu
HBAA	Co>Cu>Ni	Ni>Co>Cu	Ni>Co=Cu	Ni>Co=Cu	Co>Ni>Cu
HBAT	Co>Ni>Cu	Co>Ni>Cu	Cu>Co>Ni	Co>Cu>Ni	Cu>Ni>Co
DNSA	Cu>Ni>Co	Cu>Ni>Co	Cu>Co>Ni	Cu>Ni>Co	Cu=Co>Ni
DBSA	Cu=Co>Ni	Cu=Co>Ni	Cu=Co=Ni	Cu=Co>Ni	Cu>Co=Ni
HNA	Ni>Co>Co	Ni>Cu>Co	Cu>Co=Ni	Co>Ni>Cu	Ni>Co>Cu

TABLE - 7.10

ORDER OF MIC-VALUE OF phen-COMPLEXES IN TERMS OF METAL IONS

Ligand	Bacteria		Fungi		
	<i>S. aureus</i>	<i>E. coli</i>	<i>A. flavus</i>	<i>A. fumigatus</i>	<i>A. niger</i>
MBA	Cu>Co>Ni	Cu>Co>Ni	Cu>Co>Ni	Cu>Co=Ni	Cu>Co>Ni
DTSA	Ni>Cu>Co	Co>Cu>Ni	Co>Cu>Ni	Ni>Cu>Co	Cu>Co>Ni
PDA	Ni>Co>Cu	Ni=Co>Cu	Co>Cu>Ni	Cu=Co>Ni	Co>Ni=Cu
HBAA	Co>Ni>Cu	Co>Cu>Ni	Cu>Co>Ni	Cu>Co>Ni	Cu=Co>Ni
HBAT	Cu>Ni>Co	Cu>Co=Ni	Cu>Ni>Co	Cu>Ni>Co	Cu>Co>Ni
DNSA	Cu>Ni>Co	Cu>Ni>Co	Cu>Co>Ni	Cu=Co>Ni	Cu>Co>Ni
DBSA	Cu=Co>Ni	Cu=Co>Ni	Cu>Co=Ni	Co=Ni>Cu	Co>Ni>Cu